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SOIL SAMPLING QUALITY ASSURANCE USER'S GUIDE

by

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The inherent inseparability of a cost-effective Soil Sampling Quality Assurance/Quality Control (QA/QC) Plan from the objectives of a soil monitoring program is emphasized. Required precisions and confidence levels for the data cannot be defined until the decisions which will be made on the basis of the data are clearly stated and the consequences of making Type I (false positive) or Type II (false negative) errors are weighed. Statistical considerations are presented with special attention to analyses of variance of soil monitoring data, methods of calculating required numbers of soil samples to achieve desired precisions and confidence levels, possible applications of Kriging, and assignment of control limits to QA/QC data. The value of an exploratory or preliminary study to the cost-effective achievement of both the soil monitoring objectives and the objectives of the Soil Sampling QA/QC Plan is strongly emphasized. The value of developing a hypothetical model to estimate the distribution in space and time of soil pollutants and thus to assist in the design of the monitoring network is discussed. Methods for determination of the number and locations of soil sampling sites; sample collection methods and procedures to include frequency of sampling; sample handling to include labeling, preservation, preparation for analysis, and transport; together with QA/QC aspects are presented and discussed. Finally, the importance of systems audits and training to the achievement of soil sampling QA/QC objectives is presented and discussed.

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ABSTRACT

The inherent inseparability of a cost-effective Soil Sampling Quality Assurance/Quality Control (QA/QC) Plan from the objectives of a soil monitoring program is emphasized. Required precisions and confidence levels for the data cannot be defined until the decisions which will be made on the basis of the data are clearly stated and the consequences of making Type I (false positive) or Type II (false negative) errors are weighed. General and specific objectives for Soil Sampling QA/QC Plans are presented and discussed with special emphasis on cases associated with the management of hazardous wastes. Selected statistical considerations are presented with special attention to analyses of variance of soil monitoring data, methods of calculating required numbers of soil samples to achieve desired precisions and confidence levels, possible applications of Kriging, and assignment of control limits to QA/QC data. The value of an exploratory or preliminary study to the cost-effective achievement of both the soil monitoring objectives and the objectives of the Soil Sampling QA/QC Plan is strongly emphasized. The value of developing a hypothetical model to estimate the distribution in space and time of soil pollutants and thus to assist in the design of the monitoring network is discussed. Methods for determination of the number and locations of soil sampling sites; sample collection methods and procedures to include frequency of sampling; sample handling to include labeling, preservation, preparation for analysis, and transport; together with QA/QC aspects of all of the above are presented and discussed. The ultimate goal in the analysis and intepretation of data is to build a body of representative and comparable data on the basis of which both general guidelines (factors applicable to all sites) and specific guidelines (factors which are site-specific) may be developed for Soil Sampling QA/QC Plans. Finally, the importance of systems audits and training to the achievement of soil sampling QA/QC objectives is presented and discussed.

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CHAPTER 1

INTRODUCTION

BACKGROUND

Data resulting from any monitoring or sampling program cannot be evaluated and interpreted with confidence unless adequate quality assurance methods and procedures have been incorporated into the program design. An adequate quality assurance program requires that all sources of error associated with each step of the monitoring or sampling effort be identified and quantified.

Sources of error are then analyzed with an appropriate statistical design to yield estimates of the various components of variance. The component of variance analysis is based upon the premise that the total variance for a particular population of samples is composed of the sum of the variances from each of the identified sources of error plus an error term which is the sample to sample variance (σ^2). The population variance (σ^2) is usually unknown: therefore, it must be estimated from a set of samples collected from the population. The total sample variance (s^2) is estimated from the summation of the sum of squares (SS) from each of the identified components of variance plus the error SS. For example:

$$SS_t = SS_s + SS_p + SS_{ex} + SS_a + SS_{er}$$

where SS_t = Total SS
SS_s = Sampling SS
SS_p = Sample Preparation SS
SS_{ex} = Extraction SS
SS_a = Analysis SS
SS_{er} = Error SS

The result of this analysis provides a measure of the precision of the analysis plus confidence limits.

To date the most highly developed aspect of quality assurance undertaken in support of monitoring programs has been for the analytical procedures. Such an approach is not adequate in cases where the medium being sampled is not homogeneous, which is particularly true for soil and may also be true in some instances for air, water, sediments or foods. For example, two soil samples taken a few feet apart may differ in important characteristics or chemical pollutant concentrations by an order of magnitude or more. Therefore, quality assurance on the analytical results is a necessary but not sufficient condition for assessing total sample variability within the soil population being sampled. The analytical errors may account for a negligibly small portion of the total variance. In view of the above it is clear that for soil monitoring programs a more comprehensive quality assurance program is mandatory. This document will address the quality assurance aspects associated with soil sampling.

Prior to proceeding with the quality assurance aspects it is necessary to discuss soil monitoring in general, monitoring objectives, and possible actions which may be taken on the basis of the resulting monitoring data. Clearly it is not possible to separate the required quality assurance procedures for soil monitoring from the objectives or purposes for which the soil is being monitored.

Soil monitoring may be:

- carried out to meet the provisions and intent of environmental laws such as the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the Toxic Substances Control Act (TSCA), etc.

- source, transport or receptor oriented

- conducted to determine the presence of specified contaminants in comparison to an appropriate background level

- conducted to determine the levels of contaminant and their spatial and temporal distribution

- conducted to provide input into an exposure and risk assessment study

- part of a compliance monitoring scheme to measure the efficacy of control actions

- part of a research, technology transfer, or environmental model validation study.

Presumably, in each case where soil monitoring is deemed necessary, administrative or legal actions are likely to be taken on the basis of an evaluation and interpretation of the resulting data. The consequences of taking or not taking action must be clearly understood before it is possible to establish an allowable confidence band for quality assurance of the data. After weighing and evaluating the consequences, a value judgment must be made by a responsible official concerning the acceptable probability of making a Type I (false positive) or a Type II (false negative) error (see Chapter 3 for discussion of Type I and Type II errors). It is not possible to design a meaningful quality assurance program until this step has been taken.

The acceptable probability for each type of error must be established in relation to the consequences of making such errors and depends upon the specific objectives of the soil monitoring program. The Type I error is the error most often used in the literature. In environmental monitoring, however, the Type II error may be more important than the Type I error. The cleanup of a highly toxic spill would be an example where a false negative could create major problems for the environmental manager. The Type II error would lead the manager to conclude that a cleanup of some areas is not necessary when in fact the action levels are being exceeded and cleanup is necessary. The Type I and Type II error for the QA/QC effort should be equal to the error levels chosen for the sampling effort itself. This acceptable probability in different cases may, for example, range from 20 percent to 1 percent or less. In some circumstances the value judgment may simply be a statement of an allowable error not to be exceeded in the final data.

There may be a temptation in many cases to avoid making the necessary value judgments concerning acceptable probabilities of making different kinds of error. The course of action often substituted for the difficult value judgment is to adopt as a guiding principle the concept that one should always strive to achieve the highest precision and level of confidence (or lowest error) possible with exisiting available resources. The resulting data are then used as the basis for making decisions with the assumption that this guiding principle gives the best possible result. Obviously such an approach will rarely, if ever, be cost-effective. Two types of errors are possible. The data may be much better than required which indicates resources have been wasted, or the data may not be of adequate quality thereby resulting in costly decisions of doubtful validity. This point may be summarized by stating that resource availability is an important factor for consideration in the establishment of quality assurance programs, but resource availability should not be accepted as the sole determinant of required quality assurance methods and procedures. Maximal cost-effectiveness should be the overall goal. This generally means that a minimum adequate quality assurance plan must be defined and then implemented.

OBJECTIVES

This document is intended to serve as a user's guide presenting and explaining selected principles and applications of methods and procedures for establishing adequate quality assurance on soil sampling aspects of environmental monitoring programs. The soil sampling aspects treated include sample site selection,sample collection, sample handling, and analysis and interpretation of resulting data. No detailed treatment of analytical quality assurance procedures is given since that important aspect of the overall problem has been adequately treated elsewhere (USEPA-600/4-82-030a-d, 1982; USEPA-600/4-84-012,1984). It should be noted, however, that sampling quality assurance procedures are not fully separable from analytical quality assurance procedures. This is particularly true for sample collection and handling procedures. If an intact, timely, and representative sample of proper size and constituency is not adequately delivered to the analytical laboratory, the analytical quality assurance procedures cannot be expected to yield meaningful results. Thus the soil sampling quality assurance procedures presented here should be viewed as an important integral part of the overall quality assurance plan.

AUDIENCE

This document has been developed to serve as a user's guide for anyone designing, implementing or overseeing soil monitoring programs. It is especially applicable for personnel responsible for regulatory programs where soil monitoring is an important integral element. Special attention is given to soil sampling examples related to CERCLA since such applications are deemed to constitute high priority for soil sampling programs. Many of the principles and procedures discussed, however, are applicable to other situations as well.

APPROACH

Following the presentation in Chapter 2 of general and specific objectives of quality assurance plans a brief survey of selected applicable statistical methodology is presented.

Discussion of the value of an exploratory study to the subsequent design of a soil sampling quality assurance program leads logically into more detailed discussions of sample site selection, sample collection, and sample handling. These detailed discussions will include minimal coverage of soil monitoring protocols, per se, since they were recently treated in a comprehensive document (Mason, 1983). The focus of the discussions here will be quality assurance. The goal of each discussion will be the development of design features for sample site selection, sample collection, and sample handling to meet quality assurance objectives of defined precision and levels of confidence for each subject area.

Similarly, the goal of the discussion concerning analysis and interpretation of data will be focused on quality assurance aspects. Special attention will be focused on a technique known as the components of variance analysis. This analysis results from the use of a statistical sampling plan designed to measure as many of the sources of variation as can be identified and sampled in a cost effective manner. The analysis further identifies the amount of total sample error (or variance) that results from each component in the sampling - analysis chain. The last two subjects treated are program audits and personnel training.

To the maximum extent feasible throughout this report we will present concepts and principles first and then present selected examples of how these concepts and principles may be applied in realistic situations.

CHAPTER 2

OBJECTIVES OF QUALITY ASSURANCE-QUALITY CONTROL PLANS

INTRODUCTION

The main objective of any soil sampling quality assurance-quality control (QA/QC) plan is to determine the quality of the reported data and insure that it is adequate to the degree required for the intended end use of the data. How this objective is met depends upon the purpose of the particular sampling program.

Soil is by its very nature extremely variable. Superimposed on this variability are other sources of variation or error that can be introduced into the final result by the sampling and analytical efforts. The concept of total QA/QC has been used to develop a system for assuring the quality of the results by attempting either to provide control of the various steps in the analytical process leading from sample collection to data interpretation or to provide adequate replication for statistically determining and quantifying the sources of variation or error in the chain.

QA/QC requires that each step in this chain be shown to be valid. USEPA (1976) has indicated that the quality of the data considered to be acceptable must be defined as quantitatively as possible. The variability of the soil and the requirement for a quantitative standard for acceptability requires that a statistical sampling plan be developed that assures the precision, bias, completeness, comparability, and representativeness of the sampling effort and of the resulting data.

Statistical sampling is the mechanism by which the QA/QC program can determine the sampling precision and can provide a measure of the reliability of the entire sampling effort. Buffington (1978) quotes Congressman George E. Brown Jr. as saying "no number is significant, and subsequently worthy of being recorded, without an estimate of its uncertainty." This statement should be considered when designing the QA/QC plan for a soil sampling effort.

It is not uncommon to spend considerable money on a sampling and analysis program only to find that the samples were not collected in a manner that allows valid conclusions to be drawn from the resulting data. Ku (1978) states "...the design of a proper statistical sampling scheme depends almost entirely on the purpose for which the results are going to be used. Hence, without an explicit and defined purpose for an undertaking, the design of the sampling scheme cannot be formatted for efficient data collection and for the correct interpretation of results." Skogerboe and Koirtyohann (1976) note "...cost considerations most frequently serve as the excuse for failing to carry out even the most rudimentary quality assurance checks." This failure to accept the fact that quality assurance is cost effective continues to plague the scientific community in spite of the considerable body of literature to the contrary.

QA/QC programs for analytical laboratories are widely used and accepted. These programs are strongly oriented toward the analytical process, not toward the sampling effort. This orientation was indicated by Plumb (1981) who suggested that 15 to 20 percent of the total analytical work load be dedicated to the quality control program. Of this, five percent was allocated to the sample collection effort and 15 percent to factors that were considered to be a portion of the laboratory effort. However, studies that have been done to determine the components of variance (Snedecor and Cochran, 1982; and Bauer, 1971) in final monitoring data indicate that reversing the quality control sample allocation load would not only be more cost effective but also provide a better estimate of the quality of the sampling or monitoring effort.

The component of variance analysis identifies various components of the environmental sampling scheme that influence the total variance of the samples collected. The design of the statistical study depends upon the purpose of the sampling and the method of collection. A first approximation of the total variance can be defined by the following equation (Bauer, 1971).

$$V_t=(V_s/k) + (V_a/kn),$$

where k is the number of samples, n the number of analyses per sample, kn the total number of analyses, V_t the total variance, V_a the analytical variance and V_s the sample variance.

One of the general purposes of a sampling effort should be to obtain samples with the smallest feasible V_t and thus the best available precision. Intuitively one can identify the portion of a sampling effort where the greatest gain would be made in reducing the variation in the data. Analytical programs frequently attempt to attain a precision of less than ± 1 percent.

On the other hand, sample to sample variation for soils is often on the order of 30 to 40 percent. Increasing n by one reduces the contribution from the small analytical variance but has little or no effect on the total variance, V_t. Increasing k by one reduces both the larger sampling variance and the analytical variance; thus, increasing k produces more gain in the precision of the sampling effort.

The actual data presented in Table 1 where V_s and V_a are approximately equal (Bauer, 1971) show both the impact of increasing the number of analyses while holding the number of samples constant and vice versa. These data show the gain that was previously described.

Table 2-1. EFFECT OF INCREASES IN ANALYSES AND SAMPLE SIZE

k	n	kn	V_t	s_t*
1	1	1	0.0993	0.32
1	2	2	0.0793	0.28
1	4	4	0.0693	0.26
2	1	2	0.0396	0.20
4	1	4	0.0248	0.16

* total standard deviation

This information should be considered in determining the objectives according to the steps outlined below.

GENERAL IDENTIFICATION OF THE OBJECTIVES

General

The objectives of any quality assurance effort focus primarily upon verification of the required reliability of the sampling data to support actions which will be taken on the basis of interpretation of the data. An important consideration is the percent of Type I or Type II error which will be deemed acceptable. A decision on this matter leads to the definition of required confidence levels. Reliability might be defined as the probability that a particular measure of the soil system reflects the true average value for all of the soil in a defined geographical area in which the sample was taken. This requires that the accuracy of the method, the representativeness of the sampling, and the comparability of the data be determined.

Accuracy and Comparability

The accuracy and comparability of the data are determined by the analytical laboratory working with the agency's quality assurance laboratories. Reference samples, spikes and duplicate analyses are used as part of the routine, daily QC program. The laboratories also are involved in an interlaboratory collaborative program designed to aid in evaluating the quality of the data produced by a particular laboratory using a particular method. Environmental scientists must work cooperatively with the analytical laboratory to insure that the required field samples are taken for use by the laboratory for conducting its own QC effort. The investigator is not likely to be directly involved in the determination of the accuracy of the method used by the laboratory unless he has a specific reason to further verify the laboratories' performance.

Precision and Representativeness

The precision and the representativeness of the final results are of primary concern to the investigator. Precision measures the repeatability of the results obtained from analyzing the collected soil samples. The statistical plan used to design the sampling effort should take into consideration all of the sources of variation likely to be encountered.

Representativeness of sampling has two components. First the sample taken must reflect what is present in the soil. For example if one must measure the macro structure of the soil an undisturbed block sample must be taken and carefully prepared for transport to the lab. A sample taken for analysis of metals on the other hand can be disturbed. Another example of this aspect of representativeness would be a landfill where scrap wood had been used to absorb liquids placed in the landfill. The wood is not soil and therefore should not be included in the analyses; yet, it is a major component of the pollutant source term and therefore should be measured. Thus, the objectives of the sampling will determine how the sample should be taken and handled during shipment, etc. This first aspect of representativeness is difficult to quantify because it is often quite subjective.

The second aspect of representativeness can be quantified because it is closely tied to sampling precision. This aspect addresses the reliability of the mean and the standard deviation as measures of the amount of a chemical present in a particular area. Increased sampling intensity, (spatially and/or temporally) independent sampling, sampling audits and the use of confidence maps developed by Kriging are all examples of techniques that can help insure that the sample is representative of the conditions in the area under investigation.

The sampling plan should be designed in such a way that it provides quantitative measures of both precision and representativeness. The QA/QC required levels of reliability vary with the purpose of the study. Six situations where soils are likely to be sampled as a part of the USEPA's mandated responsibilities are illustrated below. Each situation has its own QA/QC requirements. The situations are:

- preliminary site investigations
- emergency cleanup operations
- remedial response operations
- sampling for litigation purposes
- monitoring
- research or technology transfer

Preliminary Site Investigation:

The purpose of a preliminary site investigation is to provide information about a specific site that can be used in making initial management decisions, and, should further work be necessary, for designing a detailed and comprehensive monitoring program. The data collected during the preliminary study are often used to determine if a site will require further investigation. Three basic conclusions from preliminary data might be:

- No further study is needed.
- A detailed study is needed.
- A conclusion cannot be drawn without further study.

For such conclusions to be drawn there is a definite need to measure the reliability of preliminary data. However, methods that are often used could be classified as "look and see" or "quick and dirty." Many times little attention is given to statistics in sampling design, and the efforts are sometimes biased by the interests of the particular investigator. Any approach for collecting preliminary data without adequate QA/QC should be strongly discouraged as counterproductive.

Judgmental sampling is often used in the preliminary site investigation. This approach is based upon the investigator's judgment as to where the samples should be taken. Judgmental sampling may be the best approach to use if there is a limited number of samples allowed by the study plan. The major disadvantages of using judgmental sampling centers on the fact that the samples are biased and that very often little useful information on spatial variation is obtained. This approach prevents the investigator from making certain statements about the reliability of data derived from the samples collected.

On the other hand, judgmental sampling can be combined with other sampling plans in order to insure that particular aspects of the site can be addressed. For example, examination of historical data and a site visit may indicate areas where pollutants were believed to be placed and how a plume from this location may have moved in a particular direction. A sampling plan can then be designed to focus the sampling at the original disposal area and along the suspected plume axis. The exact sampling locations can then be randomly or sequentially located; the exact choice depending upon the purpose of the study.

Emergency Cleanup Operations

The emergency cleanup operation (immediate removal) has a single focus -- remove the pollutant as quickly as possible to achieve either a background level or a level that is not an unacceptable threat to human health, welfare or the environment. The principal role of QA/QC relates to a reliable determination that cleanup operations have been adequate.

The contamination may be limited in scope; e.g., a group of leaking barrels lying on the surface or a spilled tank truck. A leaking landfill, on the other hand, could present an entirely different demand on the investigator. Resources are limited for site investigations no matter what the level in the chain leading from discovery to abatement. The emergency cleanup operation often leads to one of the higher steps in the chain. Criteria for determining if the emergency cleanup operations should be elevated to either a planned removal or a remedial response operation are based to some extent on cost and the length of time required to implement the action (USEPA, 1982).

The fact that the emergency cleanup operation can lead to one of the more definitive types of monitoring operations places a demand on the investigator to collect as much information on the area as is possible within the time and resource constraints. This demand suggests that an adequate statistical design incorporating appropriate QA/QC measures should be used to provide the quality of data needed for the decisons that must be made by the On-Scene Coordinator. A decision made on the basis of data collected following a statistical design is more likely to be defensible as there is an identified measure of reliability that can be placed on the decision process.

Remedial Response Operations

As has been previously identified, the remedial response operation is one of the possible steps in an environmental cleanup process. Studies conducted under a remedial response are normally quite detailed and have the latitude to provide for a thorough soil investigation. The designs used in these situations are likely to be directed to provide not only a quantitative evaluation of the pollutant data but also a spatial evaluation as well. The remedial response operation which is designed as a permanent remedy, at times allows the investigator to develop a data base on time trends.

Many of the actions used to control the impacts of a pollutant depend upon the nature and properties of the soil at the site. The studies conducted for remedial response usually attempt to develop soil physical and chemical characterization data along with the pollutant data.

Similar to remedial response, planned removal operations may also involve extensive monitoring and sampling programs. The detail and extent of a planned removal monitoring and sampling program may be quite extensive. However, the planned removal operation is limited by time (six months), thus limiting the investigator from collecting data for time trend analysis.

Sampling for Litigation Purposes

All of the previously mentioned sampling situations have a potential for litigation. There are, however, a group of studies that are designed for specific litigation goals. Potential questions may arise in court that must be addressed by studies designed to provide specific data. Negotiations may require studies that are designed to aid in drawing conclusions and making decisions prior to taking a negotiating stance. These studies require that a good experimental design be used. Statistical designs incorporating appropriate QA/QC measures and including "chain-of-custody" procedures are one of the best ways to provide the kinds of information needed in these situations.

The litigation study is often similar to a research study in that there is a specific hypothesis that is being tested or evaluated by the investigator. Details will vary as the purpose changes. The confidence levels desired and thus the cost of the studies are usually higher than those encountered in other types of field sampling efforts.

Monitoring Studies

The purpose of a monitoring study may be routine or it may be the outcome of a negotiation process. The study is often designed to measure pollution levels and changes in spatial and temporal distributions. Evaluation of these changes may require the use of techniques such as intervention analysis or Kriging to aid in identifying patterns which may not be directly obvious from the monitoring data itself. These studies can occur over long periods of time and have a routine aspect to them.

The design of a monitoring study and the associated QA/QC procedures frequently is dictated by a negotiated settlement or by some administrative review process. Designs that are costly often have little chance of being implemented. The more efficient the design, the better the likelihood that it will be implemented. The reliability of the data combined with a measure of cost effectiveness should be the primary consideration for selecting the monitoring design. This implies that the QA/QC program design should also be minimally adequate. Too often, cost is the excuse for failing to apply even limited statistical and QA/QC criteria in the monitoring design selection process (Skogerboe and Koirtyohann, 1974).

Properly designed, quality assured, monitoring plans allow the investigator to make comparisons within a particular monitoring data base and also to make comparisons with other monitoring studies. Thus, each properly designed monitoring study can add to our overall knowledge of the environment rather than just provide data of limited reliability for a limited use.

Research or Technology Transfer Studies

These studies are by nature designed to answer specific questions. The purpose is to increase knowledge or to make a decision about some characteristics of the soil system. The experimental design should be statistically and quality controlled. Failure to provide a measure of the reliability of the data will ultimately lead to the results of the study being questioned or invalidated by peer review.

OBJECTIVES FOR BACKGROUND MONITORING

General

Generally the design of soil monitoring programs requires that the levels of defined hazardous or potentially hazardous substances and their spatial and temporal trends be measured for some specific purpose. Often it is critical not only to quantitate levels and trends but also to link the existing levels to sources. This is necessary to enable adequate control actions to be taken whenever a situation that is hazardous to human health, welfare, or the environment is identified. Often the situation is complicated by the fact that multiple sources contribute to the measured levels.

The situation is further complicated by the presence of pollutants of recent origin mixed with pollutants of past origin. This mixing becomes especially important when the investigator attempts to trace the migration from source to receptor and also in predicting what future levels are likely to be after various proposed control measures are implemented.

Identification of spatial and temporal trends along with linkage of observed measurements to sources requires that adequate background, reference or control samples be taken.

In the absence of such background samples, interpretation of the resulting data may become extremely difficult, if not impossible. The burden of proof that background samples are not necessary, for a particular soil monitoring study, rests with the principal investigator. In the absence of such proof a prudent investigator will insure that the collection of adequate background samples is included in the monitoring study design. Furthermore, some EPA regulations concerning regulatory monitoring (U. S. Code of Federal Regulations, 1983) specifically require background sampling.

Since measured levels in presumably higher concentration areas will be compared to background levels, QA/QC procedures are just as critical for the background measurements as they are for the study area measurements. Thus, for background sampling, a QA/QC procedural umbrella must cover the selection of appropriate geographical areas, the selection of sampling sites within the geographical areas, sampling, sample storage and/or preparation, sample analysis, and interpretation of the resulting data.

Under most circumstances background data will not be available for a given monitoring location. These data must be acquired either before or during the exploratory or preliminary investigation phase. The intensity of the background sampling that is undertaken depends upon the pollutants being measured, the soil characteristics and variability, the levels of pollutant likely to be found in the study area and the purpose of the study. Further discussion of the role of background studies is presented in Chapter 4.

SPECIFIC OBJECTIVES FOR MONITORING IN SUPPORT OF CERCLA

The specific QA/QC precision and confidence level objectives for any sampling study are controlled in part by the goals of the particular study. Three example situations where soil sampling will likely be undertaken are:

- hazardous materials investigations for areas such as abandoned landfills or chemical spills
- monitoring studies
- technology transfer

The data flow that can occur in each of these situations is outlined in Figures 1, 2 and 3. The data generated in each category can provide input into the development of plans and specifications for the other situations. Data that have been subjected to a good QA/QC plan can be relied upon as a resource for the development of new data.

The main area where the magnitude of the soil sampling can be controlled is in the precision required by the sampling designs. The accuracy of the sampling is unknown because the true average is not available. Repeated sampling for a high precision nevertheless must rely on the analytical accuracy obtained in the laboratory to insure that the methods used measure what is present in the soil sample. Thus the accuracy for analysis applies only to the samples while the accuracy for the study depends on the degree to which the samples are representative of the area.

The steps outlined below are designed to provide a monitoring effort with the needed sample precision and representativeness (USEPA, FR 44:233, 1979 and Bauer, 1971).

1. Identify the objectives of the study. These should reflect the specific items of information that are required to make the decisions that will follow achievement of the study objectives.

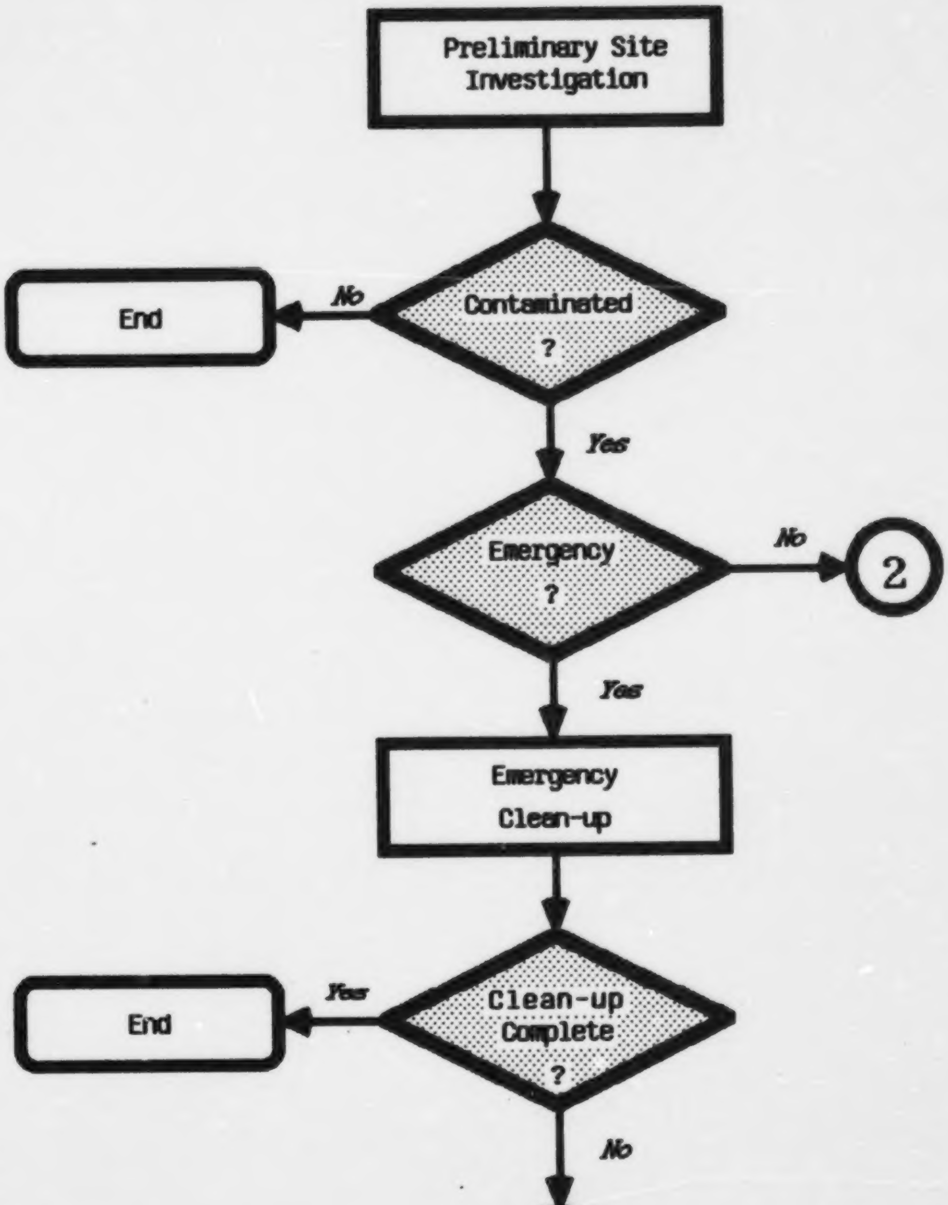

Preliminary Site Investigation
Contaminated ?
No
End
Yes
Emergency ?
No
2
Yes
Emergency Clean-up
Clean-up Complete ?
Yes
End
No
1

Figure 2-1. Data acquisition flow for hazardous materials.

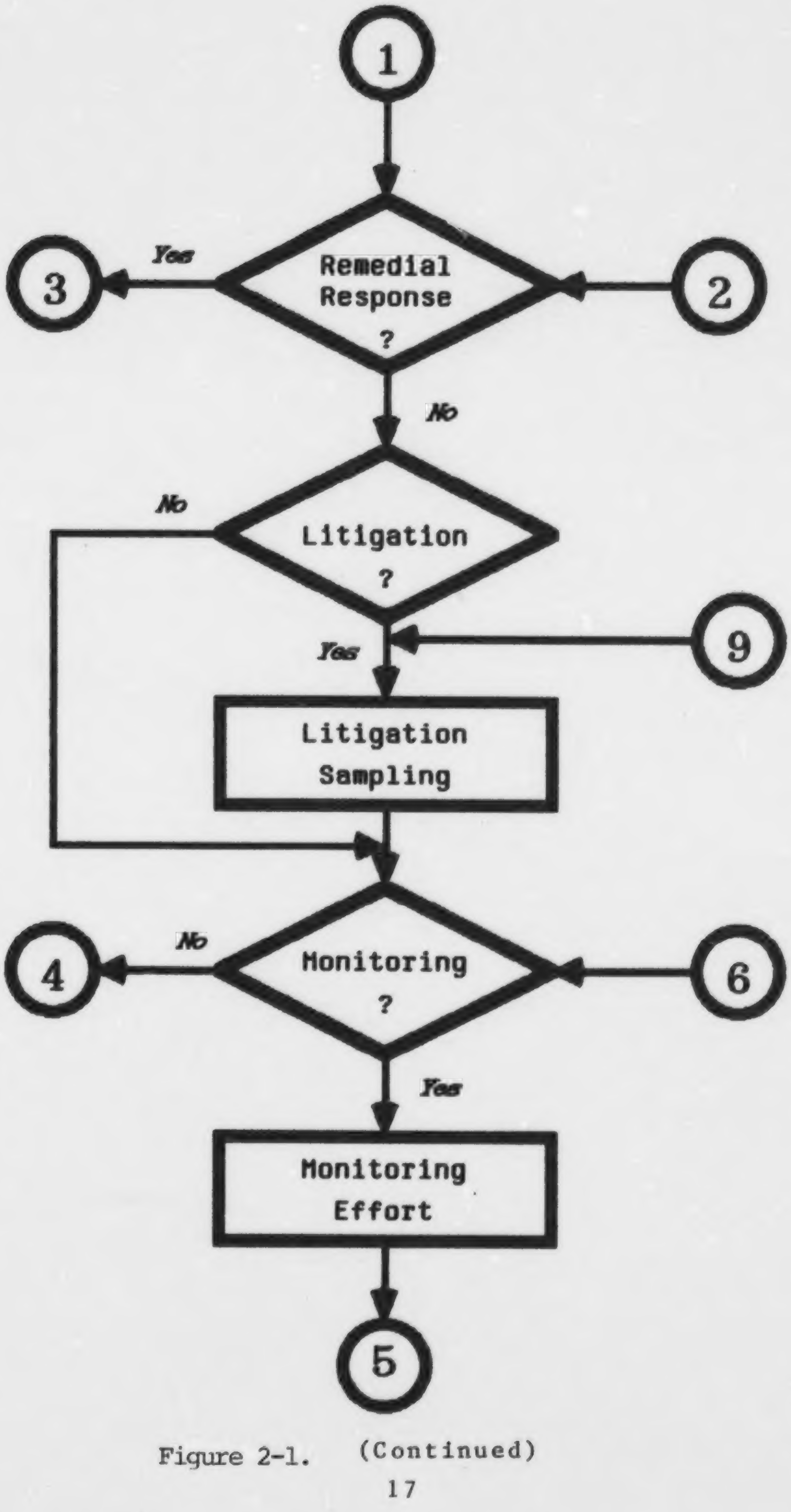

1
Remedial Response ?
Yes
3
2
No
Litigation ?
No
Yes
9
Litigation Sampling
Monitoring ?
No
4
6
Yes
Monitoring Effort
5

Figure 2-1. (Continued)

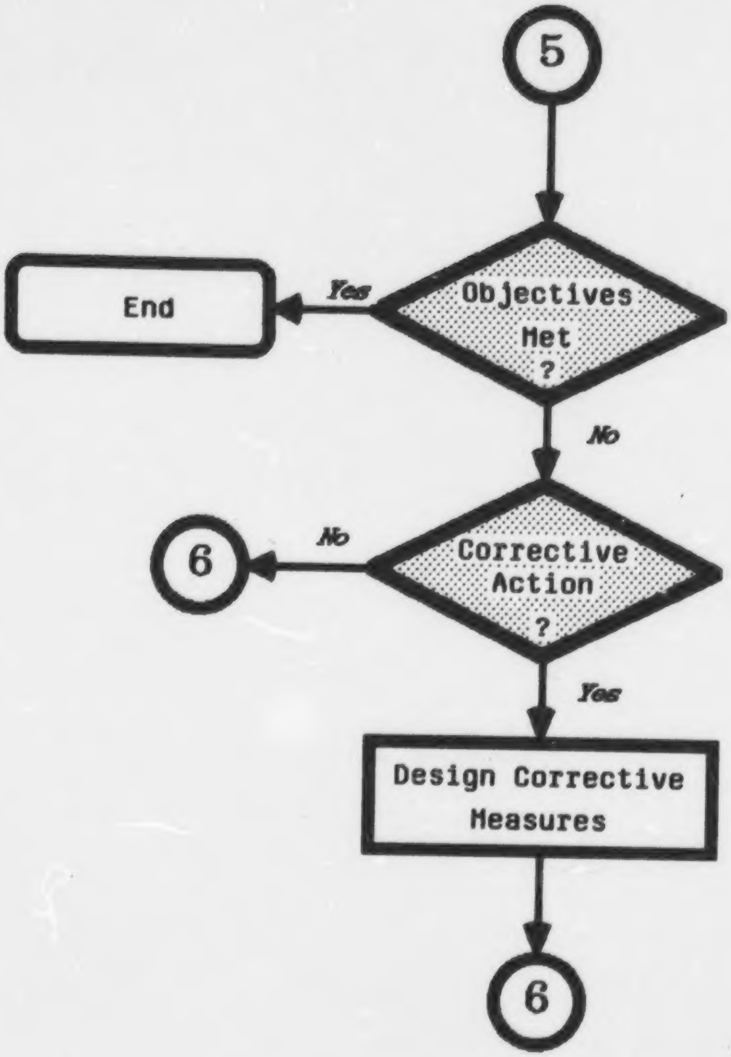
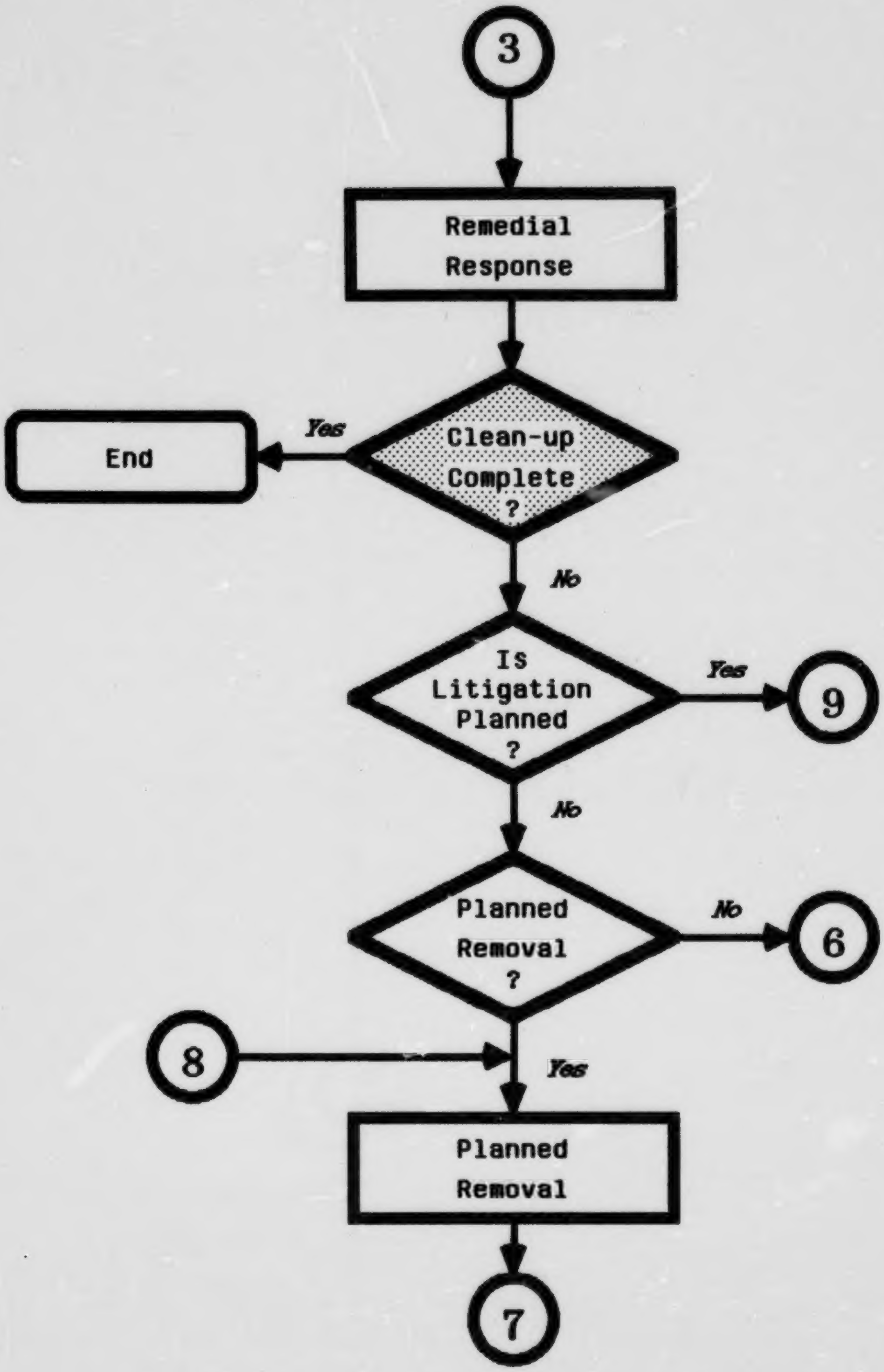

5
Objectives Met ?
Yes
End
No
Corrective Action ?
No
6
Yes
Design Corrective Measures
6

Figure 2-1. (Continued)



3
Remedial
Response
Clean-up
Complete
?
Yes
End
No
Is
Litigation
Planned
?
Yes
9
No
Planned
Removal
?
No
6
8
Yes
Planned
Removal
7

Figure 2-1. (Continued)

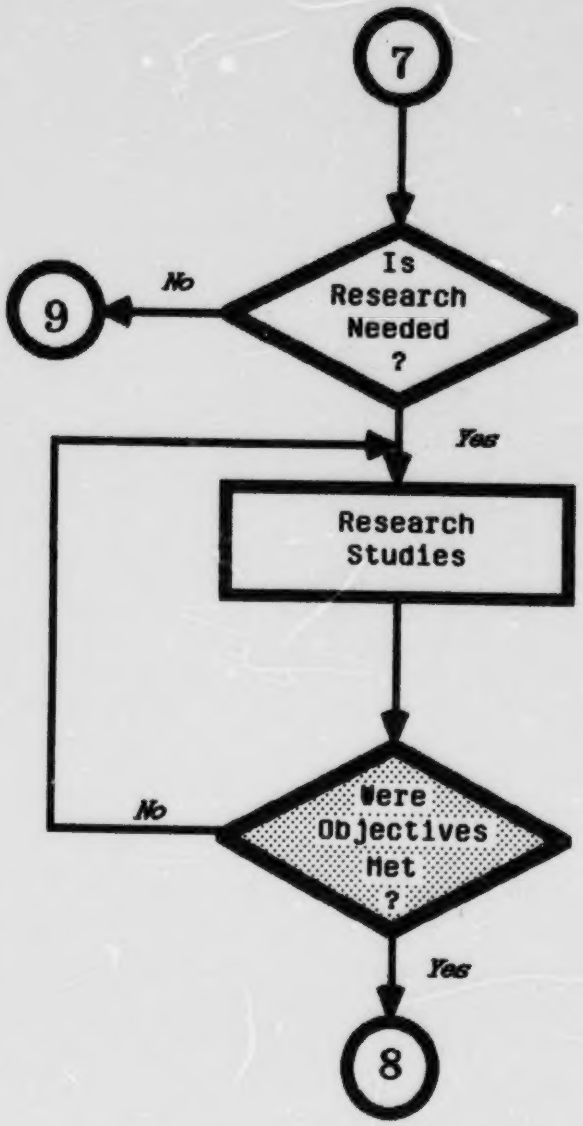

7
Is Research Needed ?
No
9
Yes
Research Studies
Were Objectives Met ?
No
Yes
8

Figure 2-1. (Continued)

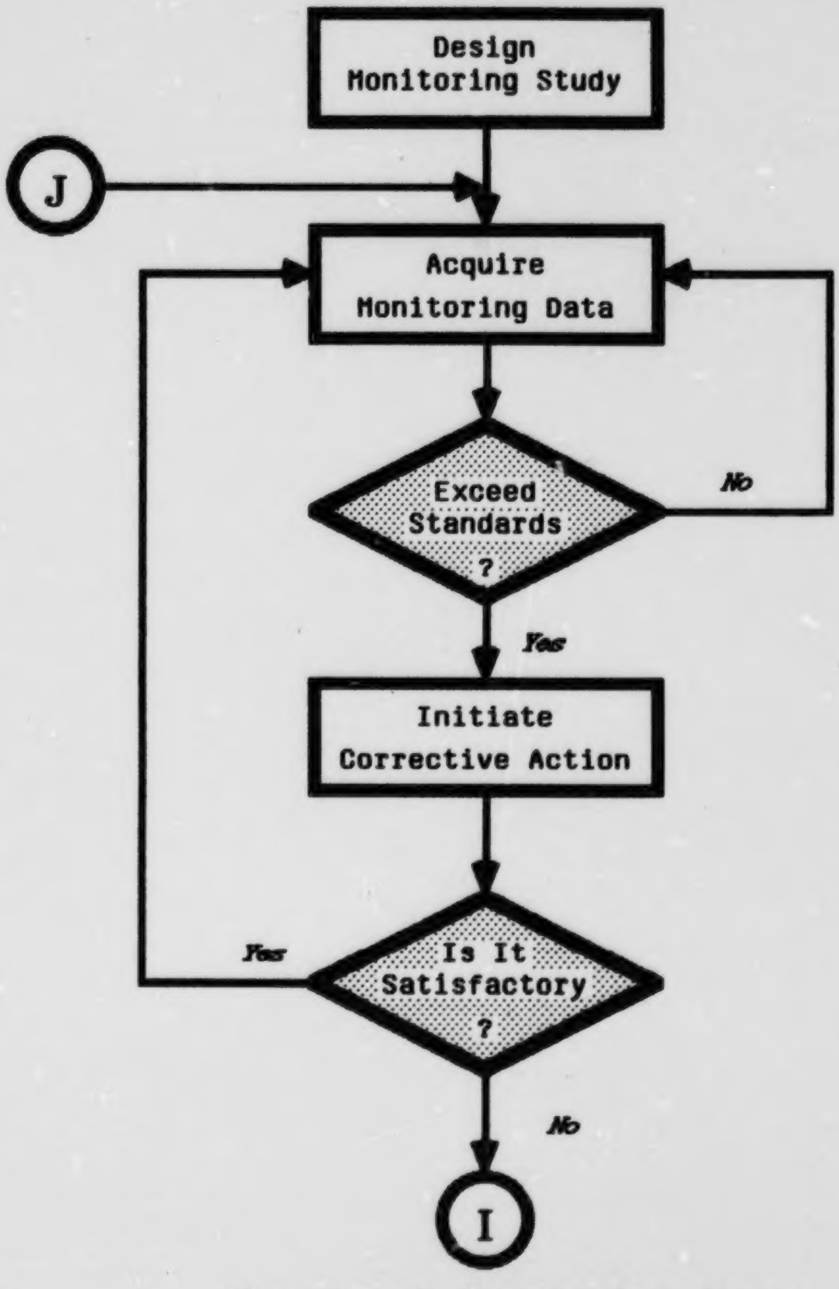

Design
Monitoring Study
J
Acquire
Monitoring Data
Exceed
Standards
?
No
Yes
Initiate
Corrective Action
Is It
Satisfactory
?
Yes
No
I

Figure 2-2. Monitoring data flow.

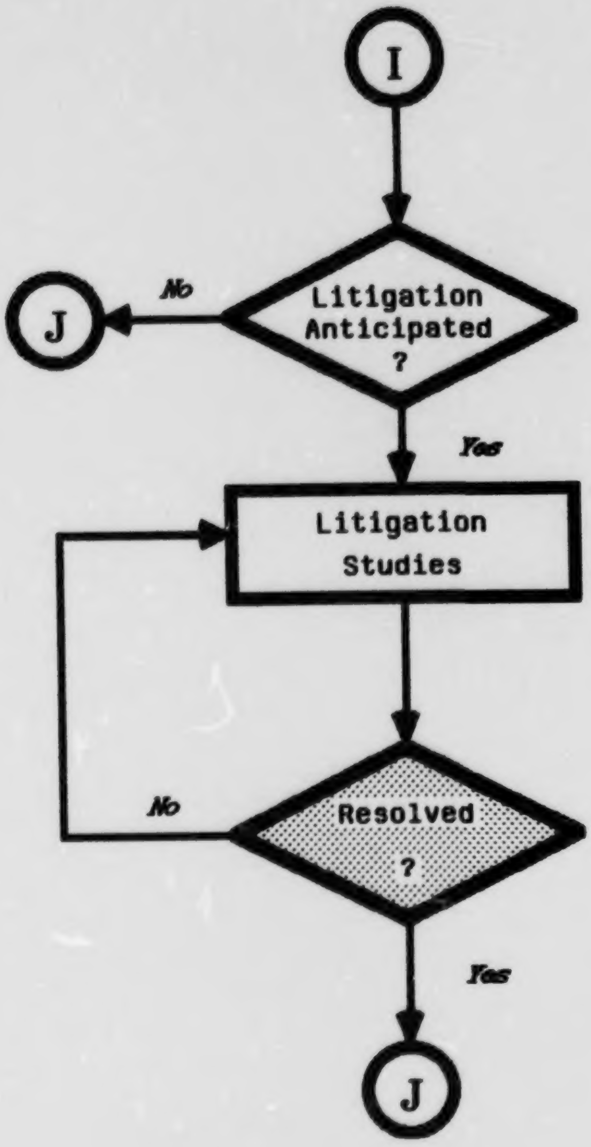

I
No
Litigation Anticipated ?
J
Yes
Litigation Studies
No
Resolved ?
Yes
J

Figure 2-2. (Continued)

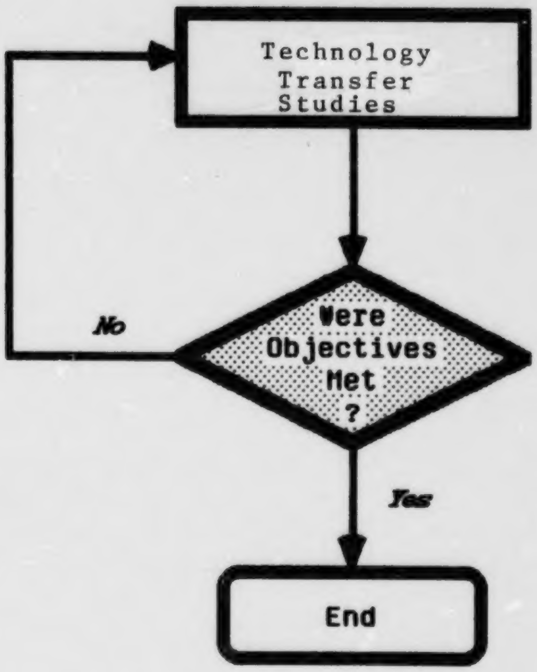

Technology Transfer Studies
Were Objectives Met ?
No
Yes
End

Figure 2-3. Technology transfer data flow.

2. Determine the components of variance that are built into the statistical design. Proper stratification of the study area will lead to several sources of variation. The sources of variation that can be controlled by the sampling are determined by the particular sampling design used and by the pattern of sample collection superimposed over the area. An analysis of variance of the data provides information which can be used in calculating components of variance. Table 3-1 gives an example of a component of variance study on a set of hypothetical soils data.

3. Choose the desired confidence level. A confidence level of 95 percent or better is desirable; however, this is often not possible because of either fundamental constraints or the economics of the situation. The investigator may have to select a level, determine the number of samples and replications required and then compare this with the resources that are available and recalculate the confidence level that can be reasonably attained with the resources available. Of course, if the revised level is not adequate to allow achievement of the study objectives, then more resources must be found, the study objectives must be revised, or the study must be abandoned. The major point to be made here is that the confidence level should be chosen before the study is conducted and not after the data are collected.

4. Obtain sampling data from other studies that have similar characteristics to the one being designed. Particularly desired data are those where the results were derived from replicated samples. These data will be used to calculate average parameters such as the coefficient of variation, variance and confidence intervals for early stages of the sampling process.

5. Calculate the mean and range of each set of replicates.

6. Group the sets of replicates according to concentration ranges and by the types of samples that are believed to be similar. An example of the groupings might be samples in the range from 0 to less than 10, and 10 to less than 25 mg/l, etc., or by soil type such as those that were in sand, silt or clay.

7. Calculate the critical difference R_c (number not to be exceeded to maintain adequate QA/QC) by noting that for any group of n duplicate analyses that are considered similar to each other, their ranges $[R_i]$ and means $[\bar{X}_i]$ can be used to

estimate the critical difference [R_C] between similar future duplicate analysis for any specific concentration level [C]. Specifically,

$$R_C = \frac{3.27 \quad (C)}{n} \sum_{i=1}^{n} \frac{R_i}{\bar{X}_i}$$

where $\bar{X}_i = \frac{x_i + x_{i+1}}{2}$ and $R_i = x_i - x_{i+1}$

8. Develop a table of R_C values for various concentrations that span the range of concentrations of interest. (A similar approach makes use of confidence limits based on the standard deviation rather than the range.) These data are used to accept or reject a set of replicated samples. The replicates are usually duplicate samples, and therefore the difference between the two values should lie within the critical range. If the sample is rejected, the analyses should be rerun if possible. The indication is that one or both of the samples or the analyses were variant. Discarding of the results should only be done after careful review of the data. There are situations in soil sampling where the coefficient of variation can reach hundreds of percent due to the variability in the soil system; therefore, the suspected outlier may in fact be a part of a wide distribution. This tends to be the case in situations where very high levels of chemicals have been spilled over small areas or where chemicals have flowed through desiccation cracks, animal burrows or old root channels. Observations made by the field party can aid in making a decision to discard a sample if appropriate comments have been noted in the log books at the time of sample collection.

9. The constructed preliminary R_C table is used until data are acquired during the sampling. As the analyses proceed the results are combined with those from previous studies. At the point where approximately fifteen pairs (USEPA, FR 44:233, 1979) of results are acquired from the particular study area a new table should be calculated based upon the average range of the data that has been accepted to date.

10. The data collected during the preliminary or exploratory site investigation and during an emergency response activity become the data base upon which later studies are evaluated and/or designed.

The specific goals of each type of study will control the required precision and confidence levels and the differences that are detectable between the samples and background. General guidelines are given below for each of the situations covered.

Preliminary Site Investigation

The preliminary or exploratory investigation is the foundation upon which many of the other studies in hazardous waste work is based. Following preliminary data evaluation a decision is made to either pursue a more definitive study or else to terminate the investigation. The reliability of data obtained from these investigations should be as high as feasible. The initial plan should attempt to set the confidence level above 95 percent. If resources limit the number of samples that can be taken, then the investigator should calculate the precision that can be attained based upon the number of samples that can be collected. If this new level of precision is deemed adequate, the study should proceed.

Using five percent duplicate samples would provide adequate QA/QC sampling under most situations (Plumb, 1981); however, there should be a minimum of two sets of duplicates in each strata sampled. Improved precision can be gained by increasing the number of replicates at each QA/QC site sampled. Analyses of splits of each of these samples provide data for within sample variation. The latter information can be delayed until later studies unless the within sample variation is expected to provide information that can be used in making decisions about the site.

When resources are limiting, a two staged sampling design may prove to be advantageous. The first stage would have a limited scope and provide only limited data. Once a decision was made that there was a possible source of pollution present, additional sampling using a higher confidence level would be initiated. The first stage could drop to a confidence level of around 80 to 90 percent. The second stage should rely on confidence levels of 95 percent or higher.

As previously stated coefficients of variation of different soil parameters can range from a low of a few percent to a high of several hundred percent. For example, a study of soil variability done by Beckett and Webster (1971) indicated that it was not uncommon for coefficients ranging from 23 to 84 percent to occur within the same soil series. The use of a precision of less than ±20 percent for parameters related to transport is probably unrealistic for any field soil sampling effort. On the other hand, parameters related to static soil properties such as percent clay, bulk density, etc., can have coefficents of variation less than ± 20 percent.

Emergency Cleanup

The emergency site sampling is designed to identify those areas where soil is contaminated and requires containment or removal. A numerical sampling criterion is usually developed for determining which areas are clean. Frequently the techniques used for making these determinations are rough field tests that lack the refinement of the laboratory analyses. Grids are often used as a basis for surveying the site. These situations offer an opportunity for more definitive information to be obtained if adequate QA/QC procedures are built into the sampling efforts.

The use of grid sampling increases the likelihood of finding the presence or absence of a chemical deposited in the soil. By adding randomly placed duplicate or triplicate sampling locations at 5 to 10 percent of the locations, the precision of the data can be determined. Sampling replication coupled with appropriate quality assurance checks in the laboratory, insures that the data meet some predetermined level of precision and accuracy.

Analyses of splits of the samples will provide data to measure the within sample variation. Replicate extractions from a subset of the samples provides a means of measuring the variation introduced by the extraction procedures. Replicate analyses of a subset of the extractions provides a measure of the analytical component of the total variance. These measures of the components of variance provide information that can be extremely valuable in designing any subsequent studies.

The need for increased precision occurs as the levels approach an assigned threshold of significance or a predetermined reference level such as a cleanup action level. A sample that is highly contaminated needs little QA/QC to determine if it exceeds background; but, a sample level close to background must have a high precision in order to detect a difference. An attempt should be made to provide a field measurement that meets a reliability that has at least a 90 percent confidence level and a precision of at least 20 percent.

Remedial Response Studies

These studies by their nature may end up in litigation; therefore, a confidence level of 95 percent or better should be used to provide the quality of data that is needed. The areas to be surveyed should be stratified and sampled according to a design that can be used to determine spatial variability as well as concentration ranges. The experimental design should provide for an identification and evaluation of the components of variance for the study situation. This requires that a suitable statistical design be formulated and that appropriate QA/QC procedures be implemented.

Studies conducted for remedial response purposes often attempt to determine pollutant behavior and pollutant distribution in order to provide a permanent remedy preventing the migration or release of hazardous substances into the environment. The experimental designs used in these cases should be reviewed by a statistician and should be focused on those areas that are required to meet the specific objectives of the study. The objectives should be distinctly defined. If several studies are being addressed with one set of samples, priorities should be set to insure that the main purpose of the study is not lost because of interference or statistical confounding.

If the sampling during exploratory or emergency response investigations has been done properly, there will be a sound basis for determining the sample size and sampling site distributions. Where pollution migration is suspected, the design will have to incorporate information on the vertical distribution as well as the horizontal distributions. It is not enough to sample the surface soil when the pollutant is expected to be moving down with the permeating water. Nested designs are required to provide the vertical components of the variation.

Planned Removal Studies

These studies are usually continuations of those initiated during emergency cleanup studies. They are conducted in more detail and should be designed to provide specific information needed to resolve control option issues. The number of replications may have to be increased if there is a need for a higher level of precision. Greater care may be required in determining the location and distribution of sampling sites in order to provide the detail that is needed to test a specific hypothesis.

An attempt at cost recovery is a likely successor to these studies. The QA/QC must be adequate in order to insure that the analytical and sampling methods and the statistical designs will withstand detailed examination that results when litigation is involved. The confidence level should be 95 percent or better and the precision should be reduced to 10 to 20 percent if possible. Preliminary data can be used to determine if this precision reduction can be accomplished within reason. A more sophisticated statistical design may have to be implemented that will provide increased precision without increasing costs (Hammond, et al., 1958).

Monitoring

Soil monitoring is often associated with measuring the changes that occur with space and time. Monitoring studies may be undertaken as part of a litigation effort or they may be undertaken in order to determine the trends in a pollutant's concentration. Precision and confidence levels will have to be adjusted to match levels required to achieve the objectives of the studies. Some form of staged or split plot design may be needed in order to be able to determine the components of variance. Techniques such as intervention analysis (Hipel, et. al., 1978) and trend line analysis will aid in determining if there have been changes in the concentration patterns over time.

CHAPTER 3

STATISTICAL CONSIDERATIONS

INTRODUCTION

This chapter reviews the role of statistics in the QA/QC process. Statistics deals with the mathematics of collection, analysis and interpretation of data. Without statistics there would be little basis for determining if a particular sample was reliable. There are numerous texts and references dealing with statistics. A number of these references have direct bearing on the collection of soil samples. The techniques presented in these references will not be discussed in detail. The user is encouraged to utilize the referenced materials if additional and/or more detailed information is required. This chapter will emphasize those techniques that have direct bearing on determining the precision of the soil sampling and the resulting analysis.

Box (1974) stated, "Environmental data are usually highly variable and it is by facing this fact, rather than running away from it, that we solve some of our problems." He gives credit to Sir Ronald Fisher for the concept that "...we can exploit the patterns of natural variation in data to design enquiries and experiments so that errors are minimized." Techniques for exploiting natural variability in soil sampling quality assurance are presented below. The basic techniques that have a bearing on soil sampling involve the use of statistical designs that are capable of providing the information needed to perform a component of variance analysis.

The component of variance analysis enables the environmental scientist to determine the amount of variation that is associated with the soil itself, and the variations associated with the collection process, handling processes such as sample shipping, storage, and preparation, and the analyses. Box (1974) sums up the role of the component of variance analyses by stating, "An appropriate study of components of variance -- how much variation is associated with chemical analysis, how much with the sampling method, how much with change of location..., together with the knowledge of how much it will cost to take a sample and perform a chemical analysis -- enables us to devise a testing scheme which can be dramatically more accurate and economical than one naively chosen." Most soil sampling efforts fail to provide for the needed statistical control and thus fall into a category of being one of the studies that Box would classify as a testing scheme that is "naively chosen."

DISTRIBUTION OF SOIL SAMPLING DATA

All statistical sampling plans are based upon the frequency distribution of the data collected by the environmental scientist and/or they are based upon the pattern that is anticipated after reviewing data collected under similar conditions. One sample collected from a location tells us little about the reliability that we can place upon the number that results from the analysis of that sample. A number of samples taken from that location provides information on the variation of the values that can be expected if all possible samples of soil were collected from the same location. The variation in the data is as much a property of the soil as is the amount of material upon which the analysis is done.

The environmental scientist can obtain information on the distribution of the values likely to be found in an area by conducting an exploratory or pilot study. The exploratory studies conducted during the initial phases of an investigation can provide an indication of the site specific frequency distribution pattern. The environmental scientist is interested in finding the location of pollutants; therefore, the pilot study should provide information on both contaminated areas and areas of background soils. EPA's Regional Laboratories and EPA's National Enforcement Investigation Center in Denver, Colorado can provide information concerning the frequency distribution of background samples and also information on the distribution of analyses performed on contaminated soils. Another source of information concerning distribution of soil pollutant concentrations is the report, Environmental Monitoring at Love Canal (USEPA, 1982).

The two most common frequency distributions encountered in the soils literature are the normal and the log-normal distributions. Where discrete events such as decay of radioactive particles occur, the Poisson distribution is the more common fequency distribution (Kempthorne and Allmaras, 1965). Rao, et al. (1979) have reviewed the frequency distribution of spatial variability for soil physical properties. They indicate that "soil properties such as bulk density, organic matter content, clay content, and soil-water content at a given tension are generally characterized by normal distributions.... However, flow related soil properties such as air permeability, saturated hydraulic conductivity, soil-water flux, pore-water velocity, and solute dispersion coefficients have been reported to be log-normally distributed." These two distributions are "the most frequently observed statistical distributions for describing the spatial variability of soil physical properties."

The distribution pattern of chemical constituents of soil including pollutants is truncated at zero. This characteristic often gives rise to a frequency curve that is skewed to the low end of the concentration scale. When this situation is encountered the data can usually be transformed to a normal distribution by taking the log of the data.

STATISTICAL DESIGNS

The design of the sampling study must be determined before the sampling is undertaken. Frequently, improper designs contain factors that are correlated with each other in such a fashion that the sampling itself determines the outcome of the investigation. This is in part avoided by proper use of randomization during the collection process. Designs such as those outlined by Mason (1983) or Peterson and Calvin (1965) can greatly aid in determining the components of variation likely to be encountered in the soil sampling effort.

The soil scientist often wants to provide information on the spatial distribution of the concentration of a particular constituent of the soil. Techniques such as those outlined by Davis (1973) for Kriging, trendline analysis, discriminant function analysis, cluster analysis and Fourier analysis provide the needed information for evaluating the spatial patterns in an area. Kriging provides one benefit that is useful from the quality assurance point of view. Kriging has the capability of providing a reliability map of the area under investigation. This map is generated from the fact that pollution samples located close to each other are often related because of their position within a pollutant plume or within their original geological deposition sequence. A series of articles by Burgess and Webster (1980a), Burgess and Webster (1980b), Webster and Burgess (1980), and Flatman (1984) give a good presentation of the use of Kriging in soil sampling and discuss the use of the error map. Mason (1982) also reviewed and described the use of Kriging and its application to soil sampling. Campbell (1978, 1979) discusses the use of discriminant function analysis and autocorrelation in evaluating the spatial distribution of soil properties.

Soil sampling faces a spatial distribution problem of another sort in the fact that sampling with depth is required of the data collection effort. Purely random samples cannot be taken once the investigator penetrates the surface of the soil as each sample is now composed of subsamples. Some form of nested design is required in order for the investigator to handle this problem. Table 3-1 shows the analysis of variance that would be undertaken for this type of soil data (Snedecor and Cochran, 1982, p. 248 with modifications).

Type I and Type II Errors

Statistical sampling plans are designed not only to measure the components of variance but also to aid the environmental manager in making informed decisions about contaminants found during an investigation of a site. The most common decision would answer the question, "Is the area contaminated or not?" The environmental scientist should design an experiment that will provide data for testing the hypothesis that the study area mean value is equal to the background mean value. Mathematically this hypothesis is expressed as

$$H_o : (\mu_S = \mu_B \mid \sigma_S^2 = \sigma_B^2)$$

where μ = mean and σ^2 = variance, the subscripts S = study area and B = background. If this hypothesis is true then there is no difference between the two areas. If the hypothesis is false then the alternate hypothesis given below is used.

$$H_a : (\mu_S \neq \mu_B)$$

The alternate hypothesis means that the two mean values are different. A similar test can be used to determine if the pollutant in the study area soils equals some action level such as a clean up level or an environmental standard.

The tests of the hypothesis are made on the basis of either the normal distribution or a normalized distribution. The hypothesis is accepted or rejected on the basis of a comparison of a sample mean with the values delineating the acceptance region (See Figure 3-1). Definition of the acceptance region includes the acceptance of a probability that the sample mean lies outside of the acceptance region (in the shaded portion of the distribution shown in Figure 3-1). This probability is defined by the significance level, the confidence level or the Type I error (all three terms are synonymous).

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The tests of the hypothesis are made on the basis of either the normal distribution or a normalized distribution. The hypothesis is accepted or rejected on the basis of a comparison of a sample mean with the values delineating the acceptance region (See Figure 3-1). Definition of the acceptance region includes the acceptance of a probability that the sample mean lies outside of the acceptance region (in the shaded portion of the distribution shown in Figure 3-1). This probability is defined by the significance level, the confidence level or the Type I error (all three terms are synonymous).

TABLE 3-1. ANALYSIS OF VARIANCE OF A NESTED SOIL SAMPLING DESIGN.

Location	Depth	Anal-1	Anal-2	Sum-Anal	Sum-Loca	Total
$i=1,\ldots,a$	$j=1,\ldots,b$	X_{ijk}		X_{ij}	$X_{i..}$	$X_{...}$
1	1	3.28	3.09	6.37		
	2	3.52	3.48	7.00		
	3	2.88	2.80	5.68	19.05	
2	1	2.46	2.44	4.90		
	2	1.87	1.92	3.79		
	3	2.19	2.19	4.38	13.07	
3	1	2.77	2.66	5.43		
	2	3.74	3.44	7.18		
	3	2.55	2.55	5.10	17.71	
4	1	3.78	3.87	7.65		
	2	4.07	4.12	8.19		
	3	3.31	3.31	6.62	22.46	72.29

I. $C = (X_{...})^2/(abn) = 72.29^2/24 = 217.7435$

II. Analysis: $\Sigma X_{ijk}{}^2 - C = (3.28^2 + .. + 3.31^2) - C = 10.2704$

III. Depths: $\Sigma X_{ij}{}^2/n - C = (6.37^2 + ... + 6.62^2)/2 - C = 10.1905$

IV. Locations: $\Sigma X_{i..}{}^2/bn - C = (19.05^2 + ... + 22.46^2)/6 - C = 7.5603$

V. Depths in Locations = III-IV=10.1905-7.5603=2.6302

VI. Analysis of Sample = II - III =10.2704 - 10.1905 = 0.0799

ANOVA TABLE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Components of Variation
Location	3	7.5603	2.5201	$V_A + nV_D + bnV_L$
Depths/Location	8	2.6302	.3288	$V_A + nV_D$
Analysis/Depths/ Location	12	0.0799	.067	V_A
Total	23	10.2704		

$n = 2, b = 3, a = 4, s^2 = 0.0067$ estimates V_A or variance due to analysis

$s_D{}^2 = (0.\ 3288 - 0.0067)/2 = 0.1610$ estimates V_D or variance due to depths

$s_L{}^2 = (2.5201 - .3288)/6 = 0.3652$ estimates V_L or variance due to location

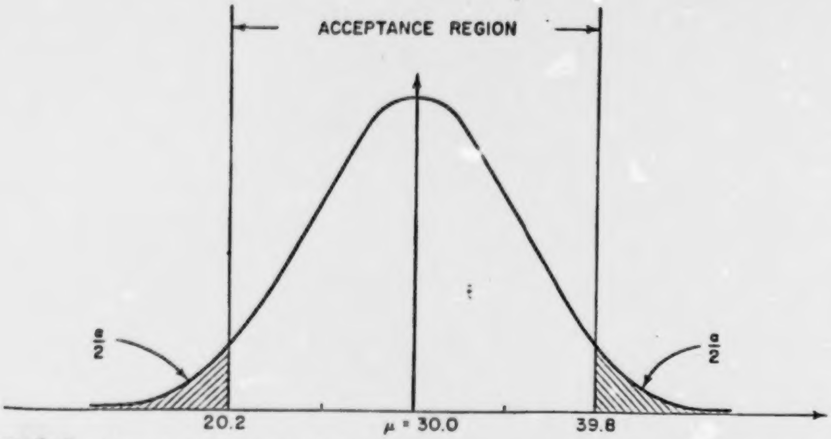
ACCEPTANCE REGION
$\frac{\alpha}{2}$
$\frac{\alpha}{2}$
20.2
$\mu = 30.0$
39.8

Fig. 3–1 Acceptance region for H: $\mu_0 = 30.0$.

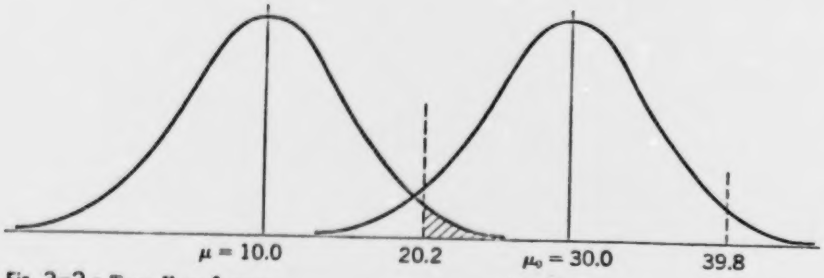
$\mu = 10.0$
20.2
$\mu_0 = 30.0$
39.8

Fig. 3–2 · Type II or β error.

The Type I error whose probability is denoted by α, is the case where we reject a hypothesis when in fact it is true. A second error called the Type II error, whose probability is denoted by β, is the case where we accept a hypothesis when in fact it is false. The values of α and β interact with each other. When α goes up β goes down. The two types of error are defined in terms of their probabilities and can be controlled to desired levels by appropriate sampling.

The Type I error is most frequently encountered in statistical tests used in the literature. The significance or confidence levels most often used are the 90, 95 and 99 percent levels. The Type II error (false negative) is also used to identify the power of the test which is equal to $(1-\beta)$.

Figure 3-1 presents the acceptance region for testing the hypothesis $H:(\mu_s = 30.0)$. The shaded portion represents the probability of a Type I error (Juran et al., 1979). Figure 3-2 shows a situation where a sample with a mean of 10 is compared with the distribution presented in Figure 3-1. Figure 3-2 is a graphic presentation of the hypothesis that the mean of our sample is equal to 30. The shaded portion of this figure represents the portion of the distribution that would give a Type II error (Juran et al., 1979).

Number and Location of Samples

One of the most useful tools for increasing the reliability of the data collection process is the replication of samples. Appendix A provides a set of tables and a graph for use in determining the number of samples needed to detect a difference between samples or to estimate the standard deviation with a precision (p) at a particular confidence level. A computer code developed by Heimbuch (1982) is also available for calculating the sample size. The location of these samples should be determined by use of some form of random selection process. However, samples are collected from a systematic grid pattern when Kriging will be employed in the analysis of the resulting data.

Further gain is made in increasing the precision of the analytical results from the sampling effort if the sample design can incorporate stratification of sampling locations. This technique makes use of the observation that certain locations tend to be similar in their properties and they in turn are different from samples taken in other locations. A typical stratification used in soil science is the soil type. Soil types are chosen because they represent an assemblage of soil units that are closely related in their physical and chemical properties.

Role of Quality Assurance in Experimental Design

The Quality Assurance Officer should be intimately involved in the review of the experimental or sampling design proposed by the investigator. He should insure that the information obtained provides measures of the components of variance that are identified in the field. An additional quality check that should be undertaken as part of the QA program is the review of the design by qualified soil scientists and other peers that are in a position to provide the necessary oversight of the sampling effort.

Broms (1980) makes the following statement; "There should be a balance between the soil investigation method, the quality of the soil samples, and the care and skill spent on the preparation and the testing of the samples. There is no point in spending time and money on careful sample preparation and on testing if the quality of the samples is poor." The QA program must address the total flow of information from the design to the reporting of the results. The sampling design is the foundation of the whole study, therefore, it should be given maximum support if the purposes of the sampling effort are to be met.

Components of Variance

The component of variance analysis provides an estimate of the sources of variation that contribute to the total variation seen in the sampling. It therefore provides an estimate of the variance of the analytical process, of the sampling and of any other factors incorporated in the experimental design. Bauer (1971) and Snedecor and Cochran (1982) discuss the use of the components of variance analysis. An excellent example of the use of this technique is provided in a report by the Electric Power Research Institute (Eynon and Switzer, 1983) on the sources of variation encountered in using the RCRA extraction procedure on utility ash. The example presented in Table 3-1 gives the components of variance for hypothetical sampling data. This technique can only be used if the design of the experiments is done in such a manner that the variation due to the parameters can be evaluated. This is accomplished by appropriate replication at each level in the design.

Compositing of Samples

One of the main techniques used to reduce sampling and analytical costs is the use of the composite sample. Combining the samples from several sampling locations reduces not only the costs but also the variation of the mean obtained by sampling. The technique is used extensively by agricultural workers when estimating the amount of fertilizer to be placed on a farmer's fields. Since the primary purpose of QA/QC is to measure the precision of the samples obtained, this technique should be avoided if at all possible. Peterson and Calvin (1965) make the following statement about this technique:

> "It should be pointed out that the composite samples provide only an estimate of the mean of the population from which the samples forming the composite are drawn. No estimate of the variance of the mean, and hence, the precision with which the mean is estimated can be obtained from a composite of samples. It is not sufficient to analyze two or more subsamples from the same composite to obtain an estimate of the variation within the population. Such a procedure would permit the estimation of variation among subsamples within the composite, but not the variation among samples in the field. Similarly, if composites are formed from samples within different parts of a population, the variability among the parts, but not the variability within the parts, can be estimated. If an estimate of the variability among sampling units within the population is required, two or more samples taken at random within the population must be analyzed separately."

Youden and Steiner (1975) caution against the use of the composite sample for much the same reasons as those outlined above. There is no measure of the precision, and therefore the reliability, of the data obtained.

Split Samples, Spiked Samples and Blanks

Split samples, spiked samples and blanks are used to provide a measure of the internal consistency of the samples and to provide an estimate of the components of variance and the bias in the analytical process.

Samples can be split to:

- Provide samples to both parties in a litigation or potential litigation situation.
- Provide a measure of the within sample variability (this is needed in order to determine the influence of other factors that may be confounded with sample splitting.)
- Provide materials for spiking in order to test recovery.
- Provide a measure of the sample bank and extraction error.

The location of the sample splitting determines the component of variation that is measured by the split. A split made in the sample bank measures error introduced at that level. A split made in the field measures field handling along with the within sample variation. A split or series of subsamples made in the laboratory for extraction purposes measures the extraction error.

Spike samples are prepared by adding a known amount of reference chemical to one of a pair of split samples. The results of the analysis of a split compared with the non-spike member of the split measures the recovery of the analytical process and also provides a measure of the analytical bias.

Spike samples are difficult to prepare with soil material itself. Frequently the spike solution is added to the extract of the soil. This avoids the problem of mixing, etc. but does not provide a measure of the interaction of the chemicals in the soil with the spike, nor does it provide an evaluation of the extraction efficiency.

Blanks provide a measure of various cross-contamination sources, background levels in the reagents, decontamination efficiency and any other potential error that can be introduced from sources other than the sample. For example, a trip blank measures any contamination that may be introduced into the sample during shipment of containers from the laboratory to the field and back to the laboratory. A field blank measures input from contaminated dust or air into the sample. A decontamination blank measures any chemical that may have been in the sample container or on the tools after decontamination is completed.

The number of QA/QC samples have been selected by a rule of thumb that one out of every twenty samples is to be assigned to each of the categories of samples. This ratio has been used successfully in several major USEPA studies (USEPA, 1982, 1984).

Table 3-2 presents the breakdown of QA/QC samples used in these previously conducted monitoring studies.

DATA ANALYSIS

The topics that follow are designed to provide insight into the use of statistical techniques for evaluating the data obtained during an investigation. They are not by any means exhaustive, but are designed to provide the basis for designing the quality assurance portions of a sampling effort and to provide the basis for obtaining the most benefit from the data acquired.

Bias

The variation seen in analytical data can be composed of variation within the sample itself, variation introduced in sample collection or preparation and variation in the analysis of the samples. The variation can further be divided into sample variation and bias. Bias identifies the component of the sampling error that causes the mean value of the sample data to be either higher or lower than the true mean value of the samples. An example of a bias would be the error in analytical results introduced by an instrument being out of calibration during a portion of the analysis. Laboratories usually introduce reference samples into their sample load in order to detect these changes. Bias in soil sampling is difficult to detect. The presence of bias can be proven by use of one of the techiques described below. On the other hand it is difficult to prove that bias is not present because the absence of bias may be the result of the inability to measure it rather than its actual absence.

Standard Additions-- It is necessary to conduct special experiments in order to detect bias in the sampling effort. The major technique used is that of adding known amounts of standard solutions to the samples: it is recommended that this be done in the field or in a field laboratory. The main problem encountered is that mixing soils to obtain homogeneity is difficult in a laboratory much less in the field. Several known quantities of the standard are added to samples taken in the field. The results should follow the equation for a straight line:

$$y = a + b_1 x$$

Bias is indicated if the data do not follow the straight line equation, or if $a \leq 0$, and if precision errors are small. If the

TABLE 3-2. QA/QC PROCEDURES FOR SOIL SAMPLES

Procedure	Comments
1. Field Blanks	One for each sampling team per day. A sample container filled with distilled, de-ionized water, exposed during sampling then analyzed to detect accidental or incidental contamination.
2. Sample Bank Blanks	The field blank, about 40% of them, passed through the sample preparation apparatus, after cleaning, to check for residual contamination.
3. Reagent Blank	One for each 20 samples to check reagent contamination level.
4. Calibration Check Standard	One for each 20 samples to check instrument calibration.
5. Spiked Extract	One for each 20 samples to check for extract matrix effects on recovery of known added analyte.
6. Spiked Sample	One for each 20 samples. A separate aliquot of the soil sample spiked with NBS Lead Nitrate to check for soil and extract matrix effects on recovery.
7. Total Recoverable	One for each 40 samples, a second aliquot of the sample is digested by a more vigorous method to check the efficacy of the protocol method.

TABLE 3-2

Procedure	Comments
8. Laboratory Control Standard	One for each 20 samples. A sample of NBS River Sediment carried through the analytical procedure to determine overall method bias.
9. Re-extraction	One for each 20 samples. A re-extraction of the residue from the first extraction to determine extraction efficiency.
10. Split Extract	One for each 20 samples to check injection and instrument reproducibility.
11. Triplicate Sample	One for each 20 samples. The prepared sample is split into three portions to provide blind duplicates for the analytical laboratory and a third replicate for the referee laboratory to determine interlab precision.
12. Duplicate Sample	One for each 20 samples to determine total random error.

units of x and y are the same, the value of b_1 should be unity; and significant deviations from unity indicates a proportional bias (Allmaras, 1965).

Occasionally a laboratory will prepare "spikes" using only the standard solutions. This should be avoided if possible because of interactions that may occur between components of the soil matrix and the chemicals under investigation. Radioactive isotopes can provide a useful indication of the recovery of the analytical process.

Internal Consistency-- If several samples of soil of different size are analyzed for a constituent, the results should fit a linear equation of the form:

$$y = a + b_2 Z$$

where "Z" is the quantity of sample analyzed. The amount of chemical detected should be directly related to the quantity of the sample analyzed. The equation should be linear; if not, bias is indicated. The "b" term depends upon the proportion of soil used. The value of "a" should not be less than zero. A negative value for "a" and a constant value for "b" indicate a negative bias. Consistency measurements can be combined with the method of standard additions in order to provide a more definitive evaluation of bias.

Analytical Procedures-- Analytical methods that make use of different basic theories can provide information on the presence of bias. This is especially true if one of the methods is considered to be the "standard" for the industry. An example from wet chemistry would be to make use of a colorimetric and a gravimetric method. Bias is present if the results of the two methods do not agree.

The use of referee laboratories can also aid in determining the reliability of the data and in detecting bias in the analysis. Techniques such as charge balance, summation of parts (more important in physical analyses), comparative values and simple examination of the data can all provide information on the analytical reliability of the sample results.

Confidence Intervals

One of the major calculations performed on the data is the calculation of the confidence interval (CI). This value is used in much of the work undertaken in QA/QC. It is used in the development of the control charts, in identifying outliers and in determining if a set of samples exceed some pre-identified standard. Two approaches can be used for calculating the intervals. Where statistical designs have been used in the sampling and analysis of the samples, the Analysis of Variance (ANOVA) provides the best method for obtaining the needed information for calculating the confidence interval. An approximation of the interval can be made by use of the range between or among two or more samples in a series. Bauer (1971) presents both techiques. When the number of replicates is limited, i.e., two or three, the range may offer a better estimate of the confidence level.

The confidence interval is bounded by the confidence limits (CL). The confidence limits are "the bounds of uncertainty about the average caused by the variability of the experiment" (Bauer, 1971). The limit is defined by the following equation.

$$CL = \bar{x} \pm ts/\sqrt{n}$$

where $\bar{x}$ = mean, s = standard deviation, n = number of samples and t = Student's t value at the desired level of confidence and n-1 degrees of freedom (See Appendix B, Table B-1, for values of t). The range can also be used to calculate the CL by using the following equation:

$$CL = \bar{x} \pm A\Sigma R$$

where ΣR = the sum of the k ranges and A = a factor derived from the relationship between the range, the standard deviation and t. The values of A are presented in Appendix B, Table B-2, but can be calculated from the following relationship:

$$A = t/c_1 k\sqrt{kn}$$

where k = the number of groups of data and n the number of samples in each group. The values of c_1 and the equivalent degrees of freedom for t are obtained from Appendix B,, Table B-3, which is based upon the relationship $s = \bar{R}/c_1$, the defining equation for the relationship between standard deviation and range.

The tolerance limits (TL) are similar to the CL but are used to identify the interval and limits into which the individuals of the population should fall. The defining equation for this value is:

$$TL = \bar{x} \pm ts$$

or

$$TL = \bar{x} \pm I\Sigma R$$

where I is a factor relating the range and the standard deviation. The value of I is obtained from Appendix B, Table B-4, or can be calculated from the relationship:

$$I = \frac{t}{kc_1}$$

Outliers

Dixon (1953, 1965) has provided techniques for identifying data points that lie outside acceptable limits and thus can be considered to be points from a different population. The differences may be due to bias, cross contamination or other factors that have altered the chemical content of the sample or the results obtained by the analysis of the sample. One technique that is identified by Bauer (1971) makes use of the range for determining if a particular value is a true outlier or merely a value on the edge of the particular distribution. the statistic

$$t_i = |x - \bar{x}| / R$$

is used to make the decision ($\bar{x}$ = mean). Appendix B, Table B-5, lists the values of t_i that are the critical values for various sample sizes.

Propagation of Errors

Consider the case where several measures (each with some associated error) are made on the same or matched samples and then an estimate is calculated from the measured values. In this case, when the measured values are statistically independent and the errors normally distributed, the following equations may be used to estimate the variances of the calculated values, where x and y represent the measured variables, s represents the standard deviation of the measured variables, and f (x) and f (x,y) represent the calculated estimates:

For Single Valued Function of an Observation:

$f(x)$	Estimated variance of $f(x)$
$\ln x$	s^2/x^2
$1/x$	s^2/x^4
$\sin x$	$(\cos^2 x)s^2$
x^p	$p^2x^{2(p-1)}s^2$

For More Than One Attribute on the Same Sample:

$f(x,y)$	Variance of $f(x,y)$
$x \pm y$	$s_x^2+s_y^2\pm 2s_{xy}$
xy	$y^2s_x^2+x^2s_y^2+2xys_{xy}$
x/y	$[s_x^2+(x/y)^2s_y^2-2(x/y)s_{xy}]/y^2$
$\ln(x/y)$	$(1/x^2)s_x^2+(1/y^2)s_y^2-(2/xy)s_{xy}$
$\ln(xy)$	$(1/x^2)s_x^2+(1/y^2)s_y^2+(2/xy)s_{xy}$

The General Case:

$f(x,y) =$

$f(\mu_x,\mu_y) + (\partial f/\partial x)_{x=\mu_x}(x-\mu_x) + (\partial f/\partial x)_{y=\mu_y}(y-\mu_y)$ + Remainder

The reference for the above is Kempthorne and Allmaras, 1965.

Testing of Hypotheses

The simplest test of hypotheses that is used is the comparison between two mean values or else the comparison between the mean and some standard value. The Student's t test is used to make the decision if the null hypothesis (H_o:($\mu_1 = \mu_2$) is true. The following equation is used to calculate the t value. This value is compared with the value of t taken from the table in Appendix B.

$$t_s = \frac{x_1 - x_2}{s(\frac{1}{n_1} + \frac{1}{n_2})^{\frac{1}{2}}}$$

$$\text{where } s = \left[\frac{n_1 s_1^2 + n_2 s_2^2}{n_1 + n_2 - 2} \right]^{\frac{1}{2}}$$

and x_1 and x_2 are the mean values of the two samples and n_1 and n_2 are the number of samples collected from the respective populations. s is the pooled sample standard deviation and s_1^2 and s_2^2 are the individual sample variances. In the example given previously, the two samples were from the background and the study area. If $t_s < t$ at an assigned confidence level for $n_1 + n_2 - 2$ degrees of freedom, then the difference between the means is not significant at that confidence level. If $t_s > t$, then the difference is significant at that confidence level.

A similar equation, given below, can be used to test the comparison between the sample mean and some action level such as a clean up level. An example of a clean up level would be the 50 ppm level used for PCB's in soil.

$$t_c = \frac{\bar{x} - AL}{s/\sqrt{n}}$$

where AL = the action level s is the standard deviation ($\sqrt{s^2}$) and n is the number of samples. A one-tailed test is used in this case because interest is only in those cases where x exceeds the action level. If the calculated t_c value exceeds the t value taken from the table in Appendix B for (n-1) degrees of freedom at an assigned confidence level, then, the hypothesis is false and the sample exceeds the action level.

Example:

A preliminary study is done in an area suspected of being contaminated with polychlorinated biphenyls (PCB's). Sixteen soil samples were collected from both the study area and from a background area. Table 3-3 lists the data and the analyses done on the data.

TABLE 3-3. PCB STUDY TO DETERMINE CONTAMINATION OF AN AREA (HYPOTHETICAL DATA)

Background Area (ppb)		Study Area (ppm)	
35.8	38.5	47.0	50.0
45.5	36.0	62.0	49.6
35.5	40.5	47.0	53.5
32.0	35.5	59.5	68.0
50.0	45.5	40.0	60.0
39.0	37.0	57.5	45.0
37.0	36.0	48.5	42.5
47.0	53.0	53.0	58.7

$\bar{x}_B = .0402$ ppm $\quad s_B{}^2 = .000037 \quad n_B = 16 \quad CV_B{}^* = \pm 15.1\%$

$x_S = 52.61$ ppm $\quad s_S{}^2 = 60.2598 \quad n_S = 16 \quad CV_S = \pm 14.8\%$

*CV - Coefficient of variation in %

This example does not need the use of statistics to determine that there is a difference between the two population means. The t value is calculated as follows:

$$s = \left[\frac{16(.000037+60.2598)}{16+16-2} \right]^{\frac{1}{2}}$$

$$s = \sqrt{32.1386} = 5.6691$$

$$t_c = \frac{52.61 - .0402}{5.6691\sqrt{2/16}} = 26.2281$$

the t value for 99 percent confidence level and a one tailed test is 2.131 for 15 degrees of freedom (dof). A value of 26.2281 is so large as to be improbable in samples of this size so the null hypothesis is rejected, i.e., the samples with mean of 52.6 come from a different population than the background samples.

A more appropriate use of this test would be to decide if the study area exceeds the 50 ppm clean up action level. The t_c value is calculated as follows:

$$t_c = \frac{52.61 - 50.00}{7.7626/\sqrt{16}} = 1.344$$

and from Appendix B, $t_{90\%,\ 15} = 1.341$;

this indicates that the study area concentration may be different from the value of 50 as this value of t_c could occur in 10 percent of the samples. Since the study area mean may exceed the 50 ppm action level, we could make the decison to clean the entire site. This is not economical because it is apparent that some locations exceed the value and others do not. A statistic can be calculated that is analogous to the tolerance limit (TL). We can assume that the standard deviation of the true mean (50ppm) equals the sample standard deviation. This yields the following equation:

$$TL' = \mu \pm Ks$$

where K = the normal deviate for the selected confidence level which may be obtained from the t table at infinite dof. Assuming a 95% confidence level the TL' becomes $50 \pm (1.96)(7.7627)$ or 34.7 to 65.2. In this case the $TL = \bar{\mu} \pm ts = 52.61 \pm (t_{95\%,15})(7.7627) = 52.61 \pm (1.753)(7.7627) = 39.0$ to 66.2 so there is little difference between TL and TL'. Only one value exceeds the 50 ppm level if one uses either the modified tolerance limit (TL') or the tolerance limit (TL).

If one decides that the upper limit cannot exceed 50 ppm under any circumstances, it would be necessary to calculate the range of values that could be considered equal to or less than 50. On the basis of the lower limit therefore all of the samples would lie within the range and would have to be removed. This latter case is the more conservative but also the more costly decision.

CHAPTER 4

EXPLORATORY STUDY

INTRODUCTION

Once objectives have been defined which involve the need for soil sampling the next step is to develop a total study protocol including an appropriate QA/QC program. In order to develop this protocol answers to the following questions must be available or estimates must be made.

- What are the likely sources of the pollutants of concern?
- How have these sources varied in the past compared to their present emissions?
- What are the important transport routes which contribute to soil contamination?
- What is the geographical extent of the contamination?
- What average concentrations of the pollutants exist at different locations and how do these vary as a function of location and time?
- Do localized areas of high concentrations exist and if so, where are they and what are their concentrations?
- Is it possible to stratify the sampling region in such a way as to reduce the spatial variations within strata?
- What are the soil characteristics, hydrogeological factors, meteorological or climatic factors, land use patterns, and agricultural practices affecting the transport and distribution of the pollutants of concern in soil?
- What is an appropriate background, or control region to use for the study.
- What are the acceptable levels of precision and both Type I and Type II errors for this study?

If detailed and specific answers to all of these questions were available in advance, there would be no need to conduct the study. The recommended approach is to conduct an exploratory study that includes both a literature and information search along with selected field measurements made on the basis of some assumed dispersion model. If one is dealing with an emergency situation such as a hazardous chemical spill, there usually will not be time to proceed in the deliberate fashion recommended here. Thus for the emergency situation it is often necessary to compress all of the planning and study design into a very short time period and then proceed to the final definitive study without delay in order to afford maximum protection to human health, welfare, and the environment. The following will assume that there is a reasonable amount of time available to conduct an exploratory study prior to the conduction of the more definitive study.

To be maximally cost effective a major element of the exploratory study is a literature and information search and an information-seeking series of interviews. Much information pertinent to the questions asked above may already be available in the published literature, in the files of governmental agencies or industrial corporations, in ongoing or completed research at local universities, or in the knowledge of local citizens. A carefully planned and organized effort should be mounted to accumulate what relevant information is available. Only after this information has been collected, collated and evaluated should any field measurements be taken. It is a good policy to adhere to a reasonable fixed period of time for the collection and analysis of available information,otherwise this process could drag on interminably. Only at the end of the fixed time period, and based on whatever information is available at that time, should the design and implementation of the field measurements portion of the exploratory study be undertaken.

Even though the principal subject of this document is QA/QC for soil sampling it is not possible to separate the QA/QC from the total soil monitoring study design. The objectives of the monitoring study are the driving force for all elements of the study design including the QA/QC aspects. The results of the exploratory study will be a set of information and field data that will serve as the basis for the design of a definitive monitoring study that includes the total integrated QA/QC program for all media. One element of this total QA/QC program will be the soil sampling QA/QC plan.

NUMBER AND LOCATIONS OF SITES FOR SAMPLING

What is desired for the final definitive study is the appropriate number of sampling sites at the appropriate locations to obtain data on the basis of which mean concentrations and standard deviations for the regions of interest may be determined. A method has been described in Chapter 3 for calculating the number of required sites in a given region if one knows the required precision, the standard deviation of the mean, and the required levels of confidence (related to acceptable levels of

Type I and Type II errors). The precision and confidence levels must be specified, usually on the basis of a value judgment by a responsible official of the agency conducting the soil sampling study. The standard deviation of the mean of the total population of soil samples in the study region must be estimated on the basis of the standard deviation of a suitable sample of the total population obtained during the exploratory study.

In general, a suitable soil sample from a number of possible soil samples may be selected on the basis of random, judgmental, or systematic sampling. A major input into selecting the optimum sampling design is the information accumulated prior to the field sampling phase. Usually the optimum approach will be a combination of judgmental and systematic random sampling. Assuming that appropriate information has been obtained in the preliminary or information-gathering phase of the exploratory study, a model may be hypothesized describing a likely spatial distributon of soil contamination as well as identifying a likely control area. Selection of a desired number and location of sampling sites on the basis of a model is a judgmental approach. Subsequently the model must be verified by collecting a limited number of samples in areas outside of the suspected contamination zone.

For example, suppose it is suspected that an abandoned hazardous waste site is leaking wastes into the groundwater. Further suppose that the groundwater is being used to irrigate crops in the vicinity. Preliminary information has identified some of the pollutants that have been placed in the waste site and has determined the hydraulic gradient extending from the site location. The recommended sampling approach is to establish a radial grid system with the center at the waste site and the zero azimuth line along the direction of the hydraulic gradient. The largest number of samples would then be taken along the zero azimuth and along the $\pm 45^{\circ}$ azimuth from zero. This is judgmental sampling. However to make sure that important data are not missed some additional samples should be taken close to the waste site along each 45° azimuth (5 additional directions). This adds systematic sampling to take care of cases where, for example, some immiscible waste constituents may be moving in a direction different from the hydraulic gradient, the hydraulic gradient has not been properly defined, or there are other sources contributing to the soil contamination. The location of the samples taken along each axis and in the pollutant plume should be selected at random.

For the selection and sampling of a control area a combination of judgmental and random sampling is recommended. Based on the available information and the assumed transport model, select a background or control region which is similar to the study area in every important aspect except for the expected absence of contamination by selected waste constituents. Select a minimum of 12-15 sampling locations at random from the background area to obtain data for calculating the mean and standard deviation of the background concentrations of selected waste constituents. It is recommended that approximately the same degree of effort go into the selection and sampling of a control area as goes into the selection and sampling of the study area.

The QA/QC program for the exploratory study need not be as stringent as that for the more definitive study. Keep in mind, however, that reasonable levels of precision and confidence must be attained in order for the resulting data to serve as an adequate foundation for further studies. As a minimum, it is recommended that duplicate samples be collected from at least 5 percent of all sampling locations and that another 5 percent of all samples be split into triplicate samples. Furthermore it is recommended that a modest number* of additional independent QA/QC soil samples be taken on a random basis at approximate mid-points between selected sampling points in regions where the hypothetical model predicts the highest concentrations will be found. Data from these additional QA/QC samples will give some measure of how well the QA/QC plan is achieving its objectives.

Duplicate sample results will help to establish precision among different samples collected from the same site. Triplicate splits of samples provide a measure of precision within a single sample, which tests the homogeneity of the sample. The additional QA/QC samples will provide data to use in evaluating possible changes in means and standard deviations when additional sampling points are added. If the two groups of samples (study design and additional QA/QC) are statistically equal, the samples can be combined. If not, then there is an indication of either some form of bias in the sampling design or one or more errors in the assumptions inherent to the sampling design. This matter must be carefully evaluated in order to determine if additional sampling is needed. In addition to the above QA/QC checks on sampling, all normal analytical QA/QC procedures such as field and trip blanks, etc., should be operative for the exploratory study.

SAMPLING AND SAMPLE HANDLING

It is assumed that an approved protocol will be followed for handling, labeling, transporting and chain-of-custody procedures for sample containers and samples.

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*Generally a number on the order of 6 to 15 should be adequate with the exact number being determined by a value judgment based on study objectives, site-specific factors, and available resources.

If appropriate approved operating procedures for these subjects are not available, then they must be prepared prior to beginning the study. Sample volumes will be specified by the analytical laboratory depending on the analytical methods to be used and the desired sensitivity. Accordingly, principal attention will be focused here on sampling methods, preparation of the samples for analysis, and QA/QC aspects of both.

Some major concerns in sampling design include identifying the required depth of sampling, whether or not sequential samples at different depths will be required, whether samples should be composited, frequency of sampling, sample preparation for analyses and QA/QC aspects of all of the above. In deciding how to deal with these concerns one must constantly keep in mind the objectives for which the soil monitoring study is being conducted. The exploratory study provides a limited opportunity to investigate some of the above subject areas experimentally to determine what effect the sampling parameters may have on the QA/QC aspects of the total study. The expenditure of modest additional resources in the exploratory study may well lead to more cost-effective designs for the final definitive study.

The sampling device used to acquire the exploratory samples should be consistent with the objectives of the final study. The simplest sampling tool should be used. Where the contaminant is believed to be on the surface, a soil punch or trowel may be used. If the contaminant is soluble or is expected to be located more than a meter below the surface a truck mounted core sampler such as a split spoon sampler should be used.

Surface sampling should be augmented with a modest number (see footnote, page 53) of sequential samples taken down to 1.5 meters in order to determine if the pollutants have moved downward. These additional samples should be located in the area of major contamination. Data from these samples will provide information for deciding if more than the surface soil needs to be sampled in the final definitive study.

With regard to compositing of soil samples, the major concerns are that the samples be representative and that high concentrations not be significantly reduced by being averaged with lower level samples. It is recommended that to improve representativeness at least four different samples taken in the vicinity of each selected sampling site be composited into a single sample. In addition a modest number (see footnote, page 53) of single non-composited QA/QC samples should be collected from sampling sites in high concentration areas for comparison of resulting data with that from composited samples.

The exploratory study is not designed to obtain information on temporal patterns in soil concentrations since the study is expected to be completed in a relatively short period of time.

Thus, temporal trends will normally be addressed in the final study. If it is possible to select a time for the exploratory study, it is best conducted at a time when the soil concentrations would be expected to be at a maximum. It may be necessary to use the hypothesized dispersion model in order to make this decision. For example, the sampling normally should not be done immediately following a heavy rain, during winds exceeding 20 knots, or during a time when the ground is frozen.

Sample preparation for analyses introduces some possibilities for errors. The sample preparation may involve drying, grinding, mixing, and sieving. Prior to any sample preparation procedures vegetation, sod, or other non-soil material must be removed from the soil fraction.

Grinding and mixing equipment as well as any sieves used must be carefully cleaned between each sample in order to avoid cross-contamination. The final rinse water used for cleaning equipment should be sampled in order to provide a sample blank for use in evaluating the decontamination efficiency. Collection of one sample blank after processing a group of 20 samples has been used successfully in a number of EPA studies (USEPA 1982, 1984). These samples should be submitted to the laboratory along with the other QA/QC samples. After evaluation of the sample blank data obtained from the exploratory study, a decision may be made to increase or decrease the frequency of blank collections.

One of the most serious possibilities for error during the sampling process is discarding vegetation, sod or other non-soil material collected with the soil sample. It is recommended that all discarded material be retained, including any materials retained on the sieve. Ten percent of these samples should be sent to the analytical laboratory for analysis with the remainder being archived. The results of these analyses will give a quantitative estimate of the possible errors introduced by removal of non-soil materials. Care must be taken in evaluating and interpreting these data as data quality will be a function of analytical capability.

ANALYSIS AND INTERPRETION OF DATA

Analysis and interpretation of the total integrated information and data resulting from the exploratory study will provide the basis for designing the final definitive monitoring study including all elements of the QA/QC plan. For example, decisions must be made on whether or not the selected control area is adequate and appropriate; whether the hypothesized model is valid; whether the study area should be stratified and if so, how; what number of samples should be collected at what locations; whether or not the QA/QC plan for sampling is adequate and if not, how it should be changed; etc.

If the exploratory study is conducted well, it will provide some data for achieving the overall objectives of the total monitoring study; it will provide data concerning the feasibility and efficacy of most aspects of the monitoring design including the QA/QC plan; it will serve as a training vehicle for all participants; it will pinpoint where additional measurements need to be made; and it will provide a body of information and data which may be incorporated into the final report for the total monitoring study.

CHAPTER 5

SELECTION OF NUMBERS OF SAMPLES AND SAMPLING SITES

INTRODUCTION

The QA/QC plan must be designed in such a way as to allow for estimation of errors in the determination of, as a minimum, mean concentrations and standard deviations of the means. In some cases the primary interest may be in the determination of a reasonable mean of extreme values (the stratum having the highest mean concentration) which must be compared to an acceptable threshold level. In the latter case protective actions will generally be required if the acceptable threshold level is deemed to be exceeded. For this case the QA/QC plan must provide data on the basis of which one may state with what confidence level the threshold action concentration is, or is not, exceeded. Both Type I and Type II errors must be taken into consideration. These errors can only be controlled by choosing an appropriate number of samples.

On the basis of data from the exploratory study the following information will be available.

- Mean concentrations and standard deviations of the means for stratified regions (assuming it was deemed necessary to stratify the study region)
- Mean concentrations and standard deviation of the mean for the control region
- Results of tests, at specified confidence levels, to determine whether or not the mean concentrations in all strata are significantly different from the control region mean concentration
- Results of tests, at specified confidence levels, to determine whether or not peak or maximum measured concentrations exceed any established threshold action levels
- Some measure, through analysis of variance tests, of the distribution of observed variances among various elements of the sampling plan, sample handling, and sample analysis

The problem now is to determine which elements of the exploratory study provide sufficient information to meet the program objectives, and where additional measurements will be necessary. Generally, since the exploratory study was designed to provide only a limited sample of the desired study population (and perhaps a biased sample) it will be necessary to obtain some additional measurements to improve the levels of precision and confidence, to confirm the results, and to expand the measurements to cover regions not previously sampled.

NUMBER OF SAMPLING SITES REQUIRED

The minimum number of samples ,n, required to achieve a specified precision and confidence level may be estimated by use of the tables given in Appendix A. For values outside the range of the tables the following equations may be used (Mason, 1983):

$$n = \frac{t^2_{(\alpha/2,n-1)}(\sigma)^2}{p^2} \quad \text{or its equivalent} \quad n = \frac{t^2_{(\alpha/2,n-1)}(CV)^2}{p^2}$$

where σ is the standard deviation of the mean for the total population, p is the precision and must be in the same units as σ, the confidence level is $1-\alpha$, and $t_{\alpha/2,n-1)}$ is the value of Student's t distribution for the two-tailed test at n-1 degrees of freedom. In the second equation CV is the coefficient of variation and if CV is in percent, p must be in percent. These equations must be solved by iteration or graphically since t is a function of n-1. Normally the two-tailed t test is used unless the objective of the study is to determine whether or not a defined value is exceeded. In the latter case a one-tailed t test is used and $t_{\alpha,n-1}$ is substituted for

$$t_{\alpha/2,n-1}$$

The tables in Appendix A are labeled to make them applicable for both one and two-tailed tests.

If one approximates the population mean μ by a sample mean, $\bar{x}$, obtained from the exploratory study, it is possible to calculate the required number of samples to achieve a specified precision at a specified confidence level. The next problem is to estimate what sources of error may be involved in proceeding in this fashion.

First, this entire approach assumes that the measurements are independent of one another and are distributed normally. If one or the other, or both, of these assumptions is not valid, undetermined errors may be introduced. Furthermore the standard deviation, s, of the sample obtained in the exploratory study may not be a good approximation of the standard deviation, σ, of the entire population. This problem can be evaluated by comparing the standard deviation obtained in the final definitive study to the one obtained from the exploratory study and testing to see if they are different at some prescribed level of confidence.

If the normal distribution assumption is not valid, then an assumption of a log normal distribution may suffice. If the measurements are dependent on one another, it may be possible to replace classic statistical techniques with Kriging. Examination of the data collected from the exploratory study should enable one to make decisions on these matters.

If one of the objectives of the final definitive study is to compare measured peak values to an acceptable threshold level, another possible source of error must be dealt with. This source of error is addressed by modifying the equation so that the minimum sample size, n, is given by the following formula (USEPA, Dallas Lead, 1984):

$$n = \frac{t^2_{(\alpha+\beta,n-1)}\sigma^2_d}{p^2_d} \quad \text{or its equivalent } n = \frac{t^2_{(\alpha+\beta,n-1)}(CV)^2_d}{p^2_d}$$

Where α = probability of a Type I error, β = probability of a Type II error, σ_d = standard deviation of the differences between all points in the strata having the highest mean concentration and the acceptable threshold value, p_d = minimum value of the difference considered to be above the threshold value, and $t_{(\alpha+\beta,n-1)}$ is the value of Student's t distribution needed for the one-tailed test at n-1 degrees of freedom. Note that if the study region is stratified, this sample size would be applicable only to the stratum having the highest mean concentration.

Table 5-1 gives some examples of determinations of required minimum numbers of samples for hypothetical data of different standard deviations to achieve different levels of precision and confidence where the presented values come directly from the appropriate tables in Appendix A. Table 5-2 gives similar examples for hypothetical data to determine the required minimum numbers of samples needed to decide if an acceptable threshold value has been exceeded at different levels of precision and confidence.

Table 5-1. Number of Samples Required to Achieve an Analytical Precision (p) at a Confidence Level of (1-α)

Standard Deviation (%)	Confidence Level (%)	Number of Samples Precision (%)				
		1	5	10	50	100
1	99	10	3	2	2	1
	95	6	2	2	1	1
	90	5	2	1	1	1
5	99	166	10	5	2	2
	95	96	6	3	1	1
	90	69	5	2	1	1
10	99	664	31	10	3	2
	95	385	18	6	2	2
	90	271	13	5	2	1
50	99	–	664	166	10	5
	95	–	385	99	6	3
	90	–	271	70	5	2
100	99	–	–	664	31	10
	95	–	–	385	18	6
	90	–	–	271	3	3

Table 5-2. Number of Samples Required to Achieve an Analytical Precision (p) at a Confidence Level of (1-α) and a Power of (1-β).*

Standard Deviation (%)	Confidence Level (%)	Power (%)	Number of Samples Precision (%)				
			1	5	10	50	100
5	99	90	326	16	16	1	1
	95		215	10	4	1	1
	90		165	8	3	1	1
	99	80	251	13	5	1	1
	95		155	8	3	1	1
	90		114	6	3	1	1
	99	70	203	11	5	1	1
	95		120	6	3	1	1
	90		83	5	2	1	1
10	99	90	1302	55	16	2	1
	95		857	36	10	1	1
	90		657	28	8	1	1
	99	80	1004	43	13	2	1
	95		619	27	8	1	1
	90		452	20	6	1	1
	99	70	813	36	11	2	1
	95		619	21	6	1	1
	90		452	15	5	1	1
50	99	90	-	1302	326	16	6
	95		-	857	215	10	4
	90		-	658	165	8	3
	99	80	-	1004	251	13	5
	95		-	619	155	8	3
	90		-	452	114	6	3
	99	70	-	813	203	11	5
	95		-	471	120	6	3
	90		-	327	83	5	2

* Since β is the probability of making a Type II error (false negative), the power, or 1-β, is the probability of not making a Type II error.

An example of a sample calculation is presented below:

Suppose σ_d = 10 percent, confidence level$(1-\alpha)$ = 95 percent,

Power $(1-\beta)$ = 90 percent, and p_d = 10 percent.

Then $n = \dfrac{t^2_{\alpha+\beta,n-1}\,(10)^2}{(10)^2} = t^2_{\alpha+\beta,n-1}$.

Solution must be by iteration. Try $n_1-1 = \infty$.

Then $n_1 = t^2_{\alpha+\beta,\infty} = (t_{\alpha,\infty}+t_{\beta,\infty})^2 = (1.645+1.282)^2 = 9$.

Recalculate n_2 with $n_1-1 = 8$.

Then $n_2 = (t_{\alpha,8}+t_{\beta,8})^2 = (1.860+1.397)^2 = 11$.

Recalculate n_3 with $n_2-1 = 10$; Then $n_3 = (t_{\alpha,10}+t_{\beta,10})^2 = (1.812+1.372)^2 = 10$.

Recalculate n_4 with $n_3-1 = 9$.

Then $n_4 = (t_{\alpha,9}+t_{\beta,9}) = (1.833 + 1.383)^2 = 10 = n_3 = n$.

Thus the desired n = 10 as shown in Table 5-2.

It is usually necessary to calculate the probable total cost of the program, including all QA/QC samples. By comparing total cost to the available resources one can determine the feasibility of continuing with the study. If inadequate resources are available, either more resources must be obtained, the study objectives must be changed, or the study should be abandoned. Experience indicates that the second item, changing the study objectives, is the most likely option.

LOCATION OF SAMPLING SITES

The location of the sampling sites will depend on whether the sampling is random, judgmental, systematic, or some combination. All information and data resulting from the exploratory study should be used to assist in the location of sampling sites. Assuming that a reasonable validation of the model used for designing the exploratory study has been achieved, the study region may be stratified as deemed appropriate. An approach using a combination of judgmental and random sampling is recommended where the stratified areas to be sampled are located judgmentally, but the specific sampling sites within the stratified areas are selected on a random basis.

In the event it is impossible to obtain a sample at a randomly selected sampling location, a sample should be obtained from the closest available alternate site. For example, the selected site may be beneath an asphalt or concrete parking lot, a road, or a building. In these cases it is not recommended to use drastic measures such as jackhammers or picks to collect soil samples. Any errors introduced by moving to the closest alternate site are not apt to influence unduly the overall results.

The movement of pollutants over the surface of a site and through the soil mass may be strongly influenced by the shape of the terrain, by soil type, by geological formations, by vegetation and by land use. If any of these factors are important, the sampling design should be stratified in order to include each important factor. For example, a liquid pollutant deposited on a hill top will move down slope. Maximum concentrations are likely to occur in low areas as opposed to ridge tops. Stratification of such an area into three strata - ridge top, hill side, valley floor - is recommended. This design allows the analysis of variance to remove the variation due to these three strata from the total error term; thus, the estimated sample variance will be reduced.

Within each stratum the location of sample points should be randomly located. The number of sampling points assigned to a stratum should be assigned on the basis of the percentage of the total area located in that stratum.

Two other techniques can help to identify the location of sample sites. The use of Kriging to analyze the exploratory study data can generate an error map for the site. If the error map is generated on the basis of a desired confidence level, the areas that do not meet this level of reliability can be identified and sampled.

Geophysical measurement techniques can be used to locate plumes of pollutants under some geological conditions. The pollutant pattern identified under these conditions can be used to stratify the sampling by "plume" and "non-plume" areas. There may be the need to identify a third stratum covering an intergrade along the edges of the plume.

QUALITY ASSURANCE ASPECTS

The best QA/QC plan that can be designed on the basis of what is known about a study area and a control area may not be adequate to achieve the desired levels of precision and confidence. Accordingly, it is recommended that additional samples be included in the definitive study design that may help to determine whether or not desired levels for QA/QC have in fact been achieved. Conceptually there are at least two different approaches available to achieve this goal. If an independent (different) method is available for measuring the parameters of importance, that method can be used and the results compared to those achieved by the first method. Generally an independent method is not available for monitoring of contaminated soils. Another approach is to deliberately overdesign the study by taking and analyzing many more samples than the recommended numbers for a minimum adequate design. This is usually deemed to be undesirable because of the additional cost which it entails.

The recommended approach is a modification of the over design concept. It is suggested that a modest number (see footnote, page 53) of additional samples be taken at randomly located sites in the stratum where the highest concentrations are expected. These high concentration areas are normally identified on the basis of the exploratory study data. The data should be analyzed for that stratum both with and without the additional samples and the two results compared. The comparisons should give some indication as to whether or not the desired levels of precision and confidence were actually achieved by the original design.

CHAPTER 6

SAMPLE COLLECTION

INTRODUCTION

An important segment of the definitive studies QA/QC plan deals with sample collection. Sample collection has been covered by Mason (1983), Cline (1944) and Ford et al. (1983). This aspect of the definitive studies must be designed to meet the specific objectives. Improperly collected samples can void the entire study. The final protocol must provide guidance on such matters as sampling methods, equipment, locations for sampling, and compositing; dealing with non-soil portions of samples; dealing with the existence of animal burrows, root channels and other such anomalies in the soil being sampled; and the selection of the depth or depths that should be sampled.

The environmental scientist should be able to estimate the components of the variance, or error, associated with each element of the sample collection methods and procedures used from the data generated by the study. Evidence from the exploratory study pertinent to this estimation process should be taken into consideration. It is recommended that a minimum adequate approach be sought consistent with the objectives of the study, the resources available and the designated required levels of precision and confidence. Also an effort should be made to establish some criteria or procedures for estimating, after the fact, whether or not the sample collection elements of the QA/QC plan and objectives were satisfactorily achieved.

SIZE OF SAMPLES AND METHODS OF COLLECTION

Generally, the minimum sample volume is specified by the analytical laboratory on the basis of the selected method and required sensitivity of analysis. Of course, enough sample must be collected so that the final soil sample remaining after any non-soil materials are discarded will be adequate to meet the requirements of the analysis. Sufficient information should be available from the exploratory study to provide guidelines on approximately what percentage of the collected sample will be discarded during the analytical sample preparation process.

The method of collecting samples must take into consideration the required depth of sampling as well as required amounts. The data obtained from the exploratory study on soil concentrations at various depths should be adequate to allow a specification of required depths of sampling for the final study. The sample collection device must be adequate to obtain samples to the required depth. Mason (1983) and Ford et al. (1983) provide information on available sampling devices and procedures. The sampling device must be carefully cleaned between each use to avoid cross contamination of samples. Suggested cleaning methods are given in USEPA (Love Canal 1982, 1984). The type of device selected should be one that provides the most cost effective sample.

Frequently when collecting soil samples anomalies such as animal burrows, root channels, sand lenses, desiccation cracks and/or other factors that can alter the sample, or the collecting procedure, and affect pollutant migration will be encountered. These anomalies should be documented and noted on coring logs, in sample log books, and on sampling site description forms.

BORING LOG

When subsurface samples are being collected a boring or core log should be prepared. The log should indicate soil structural changes, stratigraphy changes, the presence of rock, sand and gravel lenses, root channels, animal burrows, debris and other factors that may be useful in interpreting the likely avenues of contaminant migration.

The forms for these logs can be designed by the investigator or can be copied from most geological field sampling texts. The form should present both a graphic and a verbal description of the soil lying below the surface.

Quality assurance can be maintained by periodic audit of the forms and by proper training of the personnel preparing the forms. Properly prepared boring logs are one of the most valuable interpretive tools developed during an investigation.

FREQUENCY OF SAMPLING

The required frequency of sampling depends on the objectives of the study, the sources of pollution, the pollutants of interest, transport rates, and disappearance rates (physical, chemical or biological transformations as well as dilution or the determination of dispersion). Sampling frequency may be related to changes over time, season, or precipitation. Normally little information will be obtained on sampling frequency from the exploratory study but in those cases where temporal changes are expected the final study should incorporate sampling frequency into the design. It is not uncommon for many definitive studies to be conducted over a period of one year or more.

The changes expected in the concentration of pollutants in soil are normally associated with precipitation. Precipitation may influence the movement of chemical pollutants downward and aids in decomposition. Sampling frequency associated with either major rainfall events or with an accumulated amount of rainfall can often provide valuable information on changes that are occurring.

Monitoring studies are often designed to measure the effects of some remedial measure on the site. Trends are important in these cases. The frequency of sampling should be designed to measure the changes. One approach used successfully has been to provide intensive initial sampling early in the study, then to decrease sampling frequency as the levels begin to drop. One recommended procedure would be to sample monthly for the first year, quarterly for the second year, semi annually for the next two to three years then annually thereafter.

Evaluation of the trend of the data should allow the environmental scientist to determine when the sampling frequency can be reduced or halted completely. Monthly data may provide the needed data for performing statistical tests and for determining the yearly variation within the data base.

Samples collected for evaluating trends can usually be obtained on some subset of the initial year's sampling. The major focus is mainly on the highly contaminated and on the immediately adjacent areas. The environmental scientist is primarily interested in detecting changes in these adjacent areas in order to provide early warning of a breakdown of the remedial measures.

QUALITY ASSURANCE ASPECTS

QA/QC procedures of the sample collection effort must identify and determine the magnitude of errors associated with characterizing soil contamination introduced through the sample collection effort. Audits (see Chapter 9) are perhaps the most effective tool to insure that the sampling is done correctly. Factors likely to influence the magnitude of the sample collection error are sample size, collection methods, and frequency of sampling. The most important of these are the methods of collection and the frequency of sampling.

The tools used for collecting soil samples are limited and are not likely to be sources of error. The errors most likely occur in the use made of the tool. Proper replication will insure that the precision of the procedure meets the QA/QC objectives.

Techniques such as trend line analysis or interdiction analysis will provide a means of evaluating the effectiveness of the data obtained from sampling frequency studies. The methods outlined in Chapter 4 for evaluating possible errors from compositing can prove to be a valuable tool for evaluating the use of the composite sample.

A comparison between the first samples taken and the most recent should show a decrease in pollutant concentrations unless there is a new source of pollutants, there is migration into the sampled soil or there is an error in the data. This test becomes a better indicator of errors the longer the study runs.

CHAPTER 7

SAMPLE HANDLING AND DOCUMENTATION

INTRODUCTION

The goal is to define the segment of the QA/QC plan dealing with all aspects of sample handling including the transfer of the sample from the collecting device to a suitable container, transportation of the sample, and the preparation of the sample for analysis. The importance of all these aspects of sample handling and possible errors introduced thereby will naturally vary with the sampling methods, monitoring objectives, characteristics of the soil being sampled and the physical and chemical properties of the pollutants of concern.

CONTAINER PREPARATION, LABELING, PRESERVATION, AND SAMPLE PREPARATION

The sampling protocol and the QA/QC plan must address the following factors.

- Type of container material, its size, shape and the type of lid.
- Cleaning procedures for the containers
- Decontamination procedures for sampling instruments.
- Decontamination procedures for sample bank equipment.
- Labeling scheme and log book entries
- Chain of custody procedures
- Sample preparation procedures in the field
- Sample preparation procedures at the sample bank

Due to a lack of specifically tested and recommended methods dealing with the storage, handling, construction and types of containers, cleaning and decontamination of containers, and suggested materials for container lids for soil samples it is suggested that the specifications and methods identified in USEPA, Federal Register Vol. 44 No. 233 (1979) be utilized.

Table 7-1 provides general information on recommended containers, preservation requirements, and holding times for measuring selected contaminants. Even though these procedures and methods were specifically designed and tested for water samples, they are applicable for soil sampling studies.

For sampling studies that require a large number of samples and/or extensive preanalytical sample preparation a sample bank may be established. The sample bank is the element that operates between the field sampling effort and the analytical laboratory. However, for smaller studies the sample banks responsibilities are often incorporated into the responsibilities of the field sampling team or the analytical laboratory.

If a sample bank is established, sample bank personnel can assume responsibility for the following procedures:

- Custodian for all records pertaining to the sampling, sample preparation as required, and shipment of soil samples to analytical laboratories.

- Responsibility for record filing and storing, for storing and preparation of soil samples, and for dispensing containers, sampling equipment and all custody documents such as chain-of-custody forms and sample collection and analytical tags, as required.

- Responsibility for updating and maintaining the projects' master log book, auditing the records as required, generating sample bank QC sample blanks, accepting QA/QC samples for inclusion into the analytical scheme, and for scheduling the collection of field sample blanks.

- Responsibility for completing, as required, analysis data reporting forms and for assuring that all chain-of-custody requirements pertaining to all field sampling, shipping and sample bank operations, are adhered to.

Table 7-1 Sampling Containers, Preservation Requirements, and Holding Times for Soil Samples

CONTAMINANT	CONTAINER	PRESERVATION	HOLDING TIME
Acidity	P,G	Cool, 4°C	14 days
Alkalinity	P,G	Cool, 4°C	14 days
Ammonia	P,G	Cool, 4°C	28 days
Sulfate	P,G	Cool, 4°C	28 days
Sulfide	P,G	Cool, 4°C	28 days
Sulfite	P,G	Cool, 4°C	48 hours
Nitrate	P,G	Cool, 4°C	48 hours
Nitrate-Nitrite	P,G	Cool, 4°C	28 days
Nitrite	P,G	Cool, 4°	48 hours
Oil and Grease	G	Cool, 4°C	28 days
Organic Carbon	P,G	Cool, 4°C	28 days
Metals			
Chromium VI	P,G	Cool, 4°C	48 hours
Mercury	P,G		28 days
Metals except above	P,G		6 months
Organic Compounds			
Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's nitroaromatics, isophorone, Polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Extractables (phenols)	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Purgables (halocarbons and aromatics)	G, teflon-lined septum	Cool, 4°C	14 days
Purgables (acrolein and acrylonitrate)	G, teflon-lined septum	Cool, 4°C	3 days
Orthophosphate	P,G	Cool, 4°C	48 hours
Pesticides	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Phenols	P,G	Cool, 4°C	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorus, total	P,G	Cool, 4°C	28 days
Chlorinated organic compounds	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)

Polyethylene(P) or Glass(G)
Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the analytical laboratory has data on file to show that the specific types of samples under study are stable for the longer time.
For additional information see Ford et al (1983).

The following sample bank procedures have been used successfully on a number of soil monitoring studies.

A. Issuing Supplies:

(1) The sample bank issues as required sample containers, sample collection tags, chain-of-custody forms and site description forms to the sampling teams. Sample collection tags and chain-of-custody forms are normally accountable documents; the sample bank will log the forms by numerical lot identifying the team and/or the individual responsible for the temporary custody of these documents.

(2) The sample bank may be required to store sampling equipment in a suitable environment. If sampling equipment is stored at the sample bank, issuing this equipment to the sampling teams as required will be necessary.

B. Accepting and Logging Samples:

(1) Transfer of sample custody from the sampler to sample bank personnel will normally occur at the sample bank.

(2) Before accepting custody of any samples, sample bank personnel must check all tags and forms for legibility and completeness.

  (a) All individual samples must have a completely filled out sample collection tag attached.

  (b) Every sample must be identified on the chain-of-custody form.

  (c) Each site sampled must have a completely filled out site description form.

  (d) Any discrepancy will be corrected before sample bank personnel will assume custody. If a discrepancy exists that cannot be resolved to the satisfaction of the sample bank personnel, resampling, filling out additional tags and forms, and/or revisiting the site to obtain necessary documentation may be required.

(e) All unused accountable documents as shown in Table 7-2 must be returned to the sample bank on a daily basis. However, depending upon circumstances such as a sampling team's schedule and route, accountable documents may be retained by the sampling team leader. The sample bank supervisor, however, must be aware of the situation.

(3) After the sampler relinquishes custody and the sample bank personnel assumes custody of the samples, each sample must be logged into the master log book.

Preparation of soil samples for analysis may require sample bank personnel to dry, sieve, mix and aliquot samples appropriately. The preparation procedures selected are determined by the contaminant to be measured and the analytical requirements. Various techniques and methods for mixing and compositing soils have been described by Oregon State University (1971), USEPA (1984), and Peterson and Calvin (1965).

It is inappropriate to initiate a sampling study without first consulting with analytical personnel. Collecting samples that cannot be suitably analyzed will not provide data necessary for satisfying the sampling objectives.

The possibility of errors being introduced in sample preparation procedures involving the discarding of non-soil material or of non-sieved material as well as possible losses during any grinding or drying operation has been briefly discussed in Chapter 4. The definitive study decisions concerning the non-soil fraction must be made on the basis of the data obtained from the exploratory study. For example, available data may indicate that significant contamination is in the discarded portion. If so, it is recommended that the discarded portion from ten percent of the samples collected from the area having the highest concentrations be analyzed. An estimate can then be made of the total amount of contamination being discarded by multiplying the measured concentration in the discarded material by the total amount of the discarded material. Assuming that this amount is uniformly distributed through the soil sample remaining after non-soil materials and non-sieved materials have been discarded, one can then calculate an estimated value for the potential soil sample total concentration if none of the contamination had been discarded. Comparison of this potential concentration to the actual measured concentration will enable an estimate of the possible error to be made.

TABLE 7-2. ACCOUNTABLE DOCUMENT CONTROL REQUIREMENTS

Documentation	Issued by	Numbering	Interim Responsibility	Final Responsibility
Sample Collection Tags	Sample Bank	Preserialized	Sampling Team	Sample Bank
Custody Records	Sample Bank	Preserialized	Sampling Team	Sample Bank
Field Logbooks	Sample Bank		Sampling Team	Sample Bank
Site Description Forms	Sample Bank		Sampling Team	Sample Bank
Analytical Sample Tags	Sample Bank	Preserialized	Sample Bank	Analytical Laboratory
Laboratory Notebooks	Laboratory		Analytical Laboratory	Sample Bank
Analytical Data Sheets	Sample Bank		Analytical Laboratory	Sample Bank

If the error estimated by this process exceeds acceptable limits specified in the QA/QC plan, it might be necessary to modify sample preparation procedures for the definitive study. One might consider a sample preparation procedure in which the entire collected sample (soil and non-soil materials) is extracted in the analytical laboratory. The analytical results could then be reported as amounts of contaminant per gram of mixed material. At present there is no acceptable method for proceeding in cases such as these. One problem is the lack of standard reference materials for determining and measuring errors in extraction efficiency. One solution may be to try different methods of extraction and compare the results. The final interpretation of the data must then take into consideration these estimated errors.

QUALITY ASSURANCE ASPECTS

The problem is to quantitate overall errors. The recommended procedure for verifying that the QA/QC plan is being carried out properly for this chapter's factors is a periodic audit, combined with a modest amount of extra samples and analyses related to factors discussed above.

CHAPTER 8

ANALYSIS AND INTERPRETATION OF QA/QC DATA

INTRODUCTION

One goal in the analysis and interpretation of data is to show how all aspects of QA/QC for a soil monitoring study combine to give an overall level of precision and confidence for the data resulting from the study. Another goal may be to determine whether all QA/QC procedures which were used were necessary and adequate and should definitely be incorporated into future studies of the same type. This entire evaluation must be closely linked to the objectives of the study. In summary the important questions to be answered are, "What is the quality of the data (maximum accuracy attainable)?" and also," Could the same objective have been achieved through an improved QA/QC design which may have required fewer resources?"

PRESENTATION OF DATA SUMMARIES

It is desirable to provide summarized tables of validated QA/QC data in the final report. For example, QA/QC data validation procedures used in a number of soil sampling studies reported by Brown and Black (1983) included validation of sample data sets by checking and assessing the accompanying QA/QC data. The criteria for QA/QC samples and procedures used to validate all data included:

Samples and Procedures	Example Criteria
1. Reagent Blanks	Concentrations had to be less than 0.25 g/ml^{-1}.
2. Calibration Check Standards	Recovery must be between 95% and 105% of the known value for either the first analysis or the first re-check analysis.
3. Laboratory Control Standards	Recovery must be between 90% and 110% of the known value for either the first analysis or the first re-check analysis.

Data produced by any sampling and analyzing system are affected by two types of errors; random and systematic. The accuracy of any one result then, is a function of the bias (due to systematic error) and precision (due to random error) of the collection and analysis methodology. Bias has at least two components, associated with extraction and instrument efficiency, and is assessed by the mean recovery of Calibration Check Standards and Laboratory Control Standards (LCS). The LCS check overall bias for the system; the Calibration Check Standard determines the instrumental bias.

Total random error can be assessed by analyzing duplicate samples, but it includes errors due to sample collection, sample homogeneity, sample extraction, sample composition (matrix effects) and instrumental reproducibility. These errors can be evaluated by the use of the other QC procedures stated above and are assessed by calculating the standard deviations of the various analyses.

The accuracy of analysis, i.e., bias and precision, are evaluated separately below for the two types of samples, using the following equations:

$$\text{Recovery} = \text{Amount Found}/\text{Known Amount} \tag{1}$$

$$\text{Bias (B)} = \text{Recovery} - 1. \tag{2}$$

Difference (D) = $|x_1 - x_2|$ where x_1 and x_2 are the analytical results of paired analyses and the average is:

$$\bar{D} = \frac{\Sigma_i |x_1 - x_2|_i}{n} \qquad (3)$$

and the precision is:

$$s_x = \text{Precision} = 0.8862\ \bar{D} \qquad (4)$$

where 0.8862 converts the range of two results to the standard deviation (Natrella, 1963).

If component errors are used to assess total random error, then

$$\bar{D} = (\bar{D}_1 + \bar{D}_2 + \ldots)/n \text{ and} \qquad (5)$$

$$s_x = \text{Precision} = [0.8862\ (\bar{D}_1{}^2 + \bar{D}_2{}^2 + \ldots) + s_1{}^2 + s_2{}^2 + \ldots]^{1/2}.$$

Equation (3) is suitable for use on results where the concentration varies over a very narrow range. If the concentrations found vary by an order of magnitude or more, then the difference should be normalized by dividing by the average of the two values and the precision is expressed as the coefficient of variation (CV) which is $s/\bar{x}$

$$\bar{D}_n = \sum_n (|x_1 - x_2|_i) \div \frac{(x_1 + x_2)i}{2} \qquad (6)$$

$$2 \sum_n \frac{|x_1 - x_2|i}{(x_1 + x_2)i}$$

$$CV = 0.8862\ \bar{D}_n \qquad (7)$$

One of the studies discussed by Brown and Black (1983) involved lead contaminated soils. The use and evaluation of the QC analyses for this soil monitoring study was presented as follows:

The limit of detection, approximately 0.25 μg ml^{-1}, was tested on about 10 blank analyses using a more sensitive absorbance wavelength for lead on an AAS. The result was less than 0.1 μg ml^{-1}, or 2 μg g^{-1} for sample analysis. This suggests that most of the blank analyses were less than 2 μg g^{-1}, but this cannot be stated with any confidence. The results of the QC analyses were as follows:

QC Sample	No.	Mean	S
Calibration Check Standard	150	101.5%	2.6%
Laboratory Control Standard	147	101.2%	4.1%
Field Blank (μg ml^{-1})	76	<0.25	
Sample Bank Blank (μg ml^{-1})	77	<0.25	
Reagent Blank (μg ml^{-1})	148	<0.25	
Re-extraction Analysis	17	1.7%	1.4%
Total Recoverable	144	99.8%	8.0%
Split Extract (CV)	147	0.0089	0.0079
Spiked Extract	147	99.4%	5.0%
Spiked Sample	147	100.4%	5.1%
Duplicate Aliquot(CV)	134	0.053	0.047
Duplicate Sample (CV)	129	0.189	0.168
Triplicate Analysis (CV)	220	0.144	0.128

(1) Bias: The percent recoveries indicated above for the Calibration Check Standards and LCS's suggest a small positive bias for the method of soil analysis, due principally to instrument reproducibility. The result, using Equation (2), is:

$$\text{Bias} = \text{Recovery} - 1 = 1.012 - 1 = 0.012.$$

(2) Precision: The recovery of the analyte by the analytical method compared to the "total" recoverable method was essentially equal and re-extraction of the residue left from the initial extraction indicated an additional 1.7 ± 1.4 percent recovery, also essentially equivalent. Furthermore, the results of the three types of blank analyses indicate no measurable contamination from reagents, sample collection, or sample preparation. The remaining random errors are evaluated below. Because of the wide range of concentration of lead in the samples, the coefficient of variation is used, Equation (7).

Precision (total random error) from Duplicate Sample Analysis:

CV = 0.168 or 16.8% of sample concentration.

The component random errors, summed as per Equation (5), are:

$$s_x = (0.0079^2 + 0.05^2 + 0.051^2 + 0.047^2)^{1/2} = 0.085.$$

These random errors suggest that reproducibility errors(0.0079) are small and that extract matrix, sample matrix, and sample homogeneity errors are equivalent. The sum of these errors is about half the total random error so the sampling error is essentially equal to all other errors combined.

Interlaboratory precision as calculated from the results of triplicate analyses, using Equation (7) is:

Precision = CV = 0.128 or 12.8% of sample concentration,

(3) Uncertainty: The data for bias and precision can be combined to yield the uncertainty for any reported concentration by use of the following equation:

$$U = (1 + B \pm 2\ C) \qquad (8)$$

where B is the bias, C is the standard deviation or coefficient of variation as appropriate, and 2 converts these to the 95 percent confidence limits. For soil analyses, using Equation (8) and the bias and CV derived above, the 95% confidence bounds on a reported value, x, are:

Soil result will lie between 0.676x and 1.348x $\mu g\ g^{-1}$.

It is required that the QA/QC plan ensure and document that all data collected, whether used for research or for monitoring purposes, is scientifically valid, defensible and of known precision and accuracy. The described presentation of QC data, though designed for analysis of lead in soil, can be used as a guide for other sampling and data analysis protocols and/or QA/QC plans.

Presentation of QA/QC data allows readers to verify conclusions drawn as to the reliability of the data. Such an approach also contributes to the building of a body of QA/QC and monitoring experimental data in the literature which allow comparisons to be made between and among studies. Procedures used to validate the individual data points should be presented and where some points are discarded arguments should be presented to support these decisions.

PRESENTATION OF RESULTS AND CONCLUSIONS

Special emphasis should be placed on how overall levels of precision and confidence were derived from the data. Great care must be exercised to insure that, in determining results and conclusions, assumptions are not made which were not part of the study design and which cannot be tested by data derived from the study. If portions of the study results are ambiguous and supportable conclusions cannot be drawn with regard to the total reliability of the data, that situation must be clearly stated. In that event it is desirable to include recommendations for conducting an improved study in such a way as to clarify the observed ambiguities.

QUALITY ASSURANCE ASPECTS

The adequacy of all aspects of the QA/QC plan should be examined in detail with emphasis on defining for future studies an appropriate minimum adequate plan. Some aspects of the plan actually used may have been too restrictive, some may not have been restrictive enough. Appropriate analyses and interpretation of the data should identify the actual situation.

Future soil monitoring studies should have checks and balances built into the QA/QC plan which will identify early in the study whether the plan is adequate and if necessary, allow for corrective action to be taken before the study continues. This is one of the major advantages of conducting an exploratory study along the lines outlined in this report. If there are problems with the QA/QC plan, they will often be identified in the exploratory study and be corrected before major resources are expended.

There is insufficient knowledge dealing with soil monitoring studies to state with confidence which portions of the QA/QC plan will be generally applicable to all soil monitoring studies and which portions must be varied depending on site-specific factors. As experience is gained, it may be possible to provide more adequate guidance on this subject. In the meantime it is recommended that the best approach is to assume that important factors of QA/QC plans are site-specific and to conduct an appropriate exploratory study at each new study site to verify that various aspects of the QA/QC plan are adequate to meet program objectives prior to proceeding with the final definitive study.

CHAPTER 9

SYSTEM AUDITS AND TRAINING

INTRODUCTION

The material for this chapter has been obtained primarily from USEPA Kellogg Idaho Study (1984). The first phase of an auditing program for soil monitoring projects should be the preparation of standard operating procedures (SOP) that identify the methods and techniques necessary to perform all aspects of the required audit. The SOP must be adequate to perform onsite sampling and sample bank (where applicable) audits. The second phase should then be the actual conduct of the required field audit. Audits are conducted by appropriate elements of agencies or organizations having cognizance over the monitoring project. The frequency of auditing should be determined by the project officer. Juran et al. (1979) state that, "the activities subject to audit should include any that affect quality regardless of the internal organizational location."

A system audit is an overall evaluation of a project to:

- Verify that sampling methodology is being performed in accordance with program requirements
- Check on the use of appropriate QA/QC measures
- Check methods of sample handling, i.e., packaging, labeling, preserving, transporting, and archiving in accordance with progam requirements
- Identify any existing quality problems
- Check program documentation, i.e., records (site description, chain-of-custody collection and analytical tags, field and sample bank log books and field work sheets)
- Initiate corrective action if a problem is identified

- Assess personnel experience and qualifications if required

- Follow-up on any corrective action previously implemented

- Provide onsite debriefings for sampling team and sample bank personnel.

- Provide a written evaluation of the sampling and sample bank program

The purpose of the system audit is to ensure that the QA/QC system planned for the project is in place and functioning well.

The auditor first must review Work Plans, Protocols, Test Plans, QA/QC Project Plan, and all Program Reports. A discussion of the current status of the project, and the identity of any problems encountered, with the project officer is suggested before conducting the onsite sampling audit. Sample chain-of-custody procedures and raw data are checked as appropriate and results of blind QC samples routinely inserted in the sample load by sample bank personnel are reviewed. Spot-checks of sampling methods and techniques, sampling and analysis calculations, and data transcription are performed.

SAMPLE BANK AUDIT

The primary objective is to determine the status of all Sample Bank documentation and archived samples. Emphasis is placed on:

- Verifying that the documentation is in order and sufficient to establish the disposition of any sample collected

- Determining any discrepancies that currently exist and initiating corrective action as appropriate

- Verifying that the recording of QA/QC measures (blanks, duplicate spikes, blinds) is in accordance with the QA/QC Plan

- Establishing procedures for final disposition and mechanics of transfer of all Sample Bank holdings upon termination of the operation.

The first step of the audit is to inventory the Sample Bank records and archived samples. The records that must be inspected are:

- Chain-of-custody forms
  - Field forms
  - Analysis forms
- Sample tags
  - Field tags
  - Analysis tags
- Analysis forms
  - Individual samples
  - Batch sheets
- Shipment forms
- Logbooks
  - Soils
  - Daily log

The operational procedures inspected should include:

- Preparation Procedures (sample bank or analytical laboratory)
  - Drying (if used)
  - Sieving
  - Mixing
  - Packaging
  - Shipping
- Housekeeping
  - Safety
  - Decontamination
  - Evaluation of Swipe Samples
- Security
  - Forms (documents)
  - Samples
- Storage
  - Sampling equipment
  - Archived samples

Check that required documentation has been maintained in an orderly fashion, that each of the recorded items is properly categorized, and cross-checking can be easily performed. In addition, ensure that data recording conforms to strict document control protocols and the program's QA/QC Plan.

The archived samples inspected can be categorized as follows:

- Soil
- Blanks
- Splits
- Standard Reference Materials (SRM)
- Non-Soil Materials Collected with the Soil Sample

Conduct an audit of the archived samples. Verify that appropriate samples exist for each entry in the logbook. Field sample tags should be replaced by the appropriate analytical tags, and chain-of-custody forms are prepared in order to transfer the samples. Detailed sample bank procedures are presented by USEPA Dallas Lead Study (1984).

DAILY LOG

Check for clear, concise entries detailing events of the day (such as numbers of samples processed), problems encountered, and actions taken to solve them. This log can provide excellent documentation of the operation of the Sample Bank.

SAMPLE BANK LOGS

Review these logs for complete sample information entered. Changes made should be by crossing out so the original entry is still visible, and initialing. In addition checks for the identification and documentation of split and duplicate samples, and field and Sample Bank blanks must be performed.

SAMPLE COLLECTION AUDITS

It is recommended that an audit of the overall QA/QC plan for sample documentation, collection, preparation, storage, and transfer procedures be performed just before sampling starts. The intent of this audit is to critically review the entire sampling operation to determine the need for any corrective action early in the program. Additional total program or partial audits can be conducted at various times throughout the sampling program.

It is recommended that the Project Officer maintain a QA/QC Coordinator onsite during sample collection to monitor the sampling team's activities, provide technical and corrective action suggestions to the sampling teams, and supplement performance audits on sampling as needed.

FIELD AUDITS

The primary objective is to determine the status of sampling operations. Emphasis is placed on:

- o Verifying that operational aspects and procedures are in accordance with the protocols and QA/QC plan.
- o Verifying the collection of all samples including duplicates and field blanks.
- o Verifying that documentation is in order and sufficient to establish the collection location of any sample collected.
- o Determining discrepancies that exist and initiating corrective action as appropriate.
- o Collecting independent samples.

The on-site field audit is to inspect sample records and equipment. Records inspected include:

a. Chain-of-Custody Forms

b. Sample Tags

c. Site Description Forms

d. Log Books

The operational procedures inspected should include:

- o Sampling Procedures
  - Equipment
  - Techniques
  - Decontamination
  - Collection of duplicate and field blank samples
  - Security
  - Sample storage and transportation
  - Containers
  - Contaminated waste storage and disposal
  - Site Description Form entries

DATA MANAGEMENT AUDITS

An audit of the data management system by tracing the flow of specific samples through the system should be performed. In particular, the ability of the system to correctly identify a sample from any one of its identification numbers should be checked.

Entries in the sample bank's logbook will be the basis for these performance checks. From time to time, erroneous input information may be used to audit the system.

TRAINING

The project leader of a soil monitoring project is responsible for ascertaining that all members of his project team have adequate training and experience to carry out satisfactorily their assigned missions and functions. Until a field sampling team has worked together long enough for the project leader to have verified this from first hand knowledge it is good practice, in addition to any classroom training or experience, to conduct comprehensive briefing sessions for all involved parties during which all aspects of the sampling protocol, including the QA/QC plan, are presented and discussed in some detail. This approach will help the project personnel to develop into a team where each team member knows his own job well and knows how it fits into the overall team effort. Sufficient field training exercises should follow the briefing sessions until each team member can demonstrate successfully that he can perform his job routinely well and without delay. Of course, on subsequent projects of the same general type with the same team, the training exercises may be reduced in number or dispensed with as deemed appropriate by the project leader.

In summary, the sampling effort must include classroom and field training programs that have provided detailed instruction and practical experience to personnel in sample collection techniques and procedures, labeling, preservation, documentation, transport, and sample bank operational procedures. Also, special training programs concerning procedures and program documentation should be completed by all personnel prior to their involvement in the conduction of any audits.

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APPENDIX A
TOOLS FOR ESTIMATING NUMBER OF SAMPLES TO ACHIEVE SPECIFIED LEVELS OF PRECISION AND CONFIDENCE

The graph, shown as Figure A-1, can be used to determine the number of samples required to estimate the standard deviation within a stated percent of its true value with confidence levels of 90, 95 and 99 percent. A series of tables are also presented which provide estimates of the number of samples necessary to achieve a specified level of confidence for both single-tailed (75-99.5%) and two-tailed (50-95%) t tests. The precision is to be stated and it is assumed that the coefficient of variation is known.

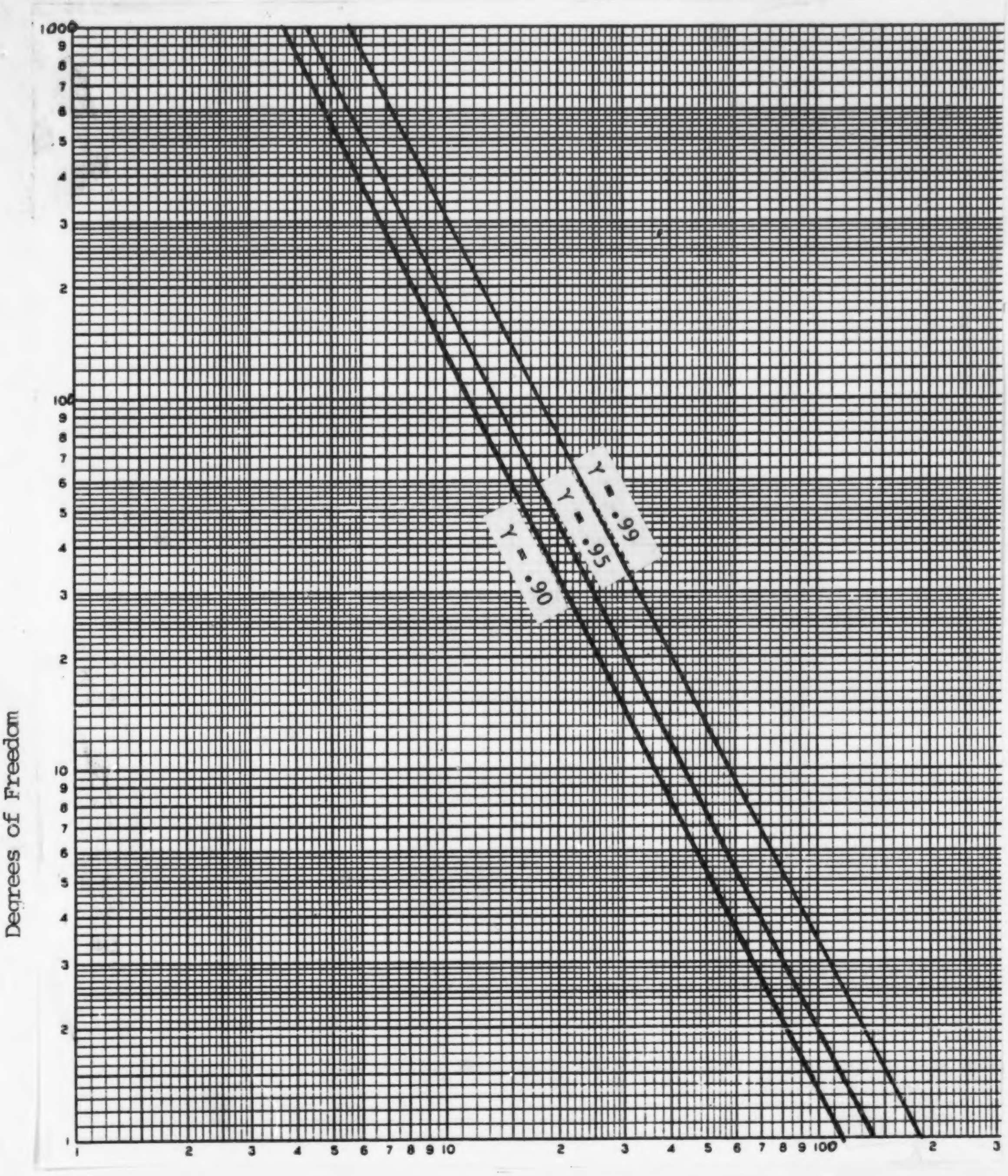

Figure A-1. Number of degrees of freedom required to estimate the Standard Deviation within P% of its True Value with confidence level γ.

TABLE A-1. ESTIMATED NUMBER OF SAMPLES TO ACHIEVE SPECIFIED LEVELS OF PRECISION AND CONFIDENCE WHEN COEFFICIENT OF VARIATION (CV) IS KNOWN.

Confidence Level
50(%): two-tailed t test
75(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	1	1	1	1	1	1	1	1	1	1	1	1
2	3	1	1	1	1	1	1	1	1	1	1	1
4	8	3	1	1	1	1	1	1	1	1	1	1
6	17	5	2	1	1	1	1	1	1	1	1	1
8	30	8	2	1	1	1	1	1	1	1	1	1
10	47	12	3	1	1	1	1	1	1	1	1	1
20	182	47	8	3	2	1	1	1	1	1	1	1
30	410	104	17	5	3	2	2	1	1	1	1	1
40	728	182	30	8	4	3	2	2	1	1	1	1
50	1138	285	47	12	6	4	3	2	2	1	1	1
100	4550	1138	182	47	21	12	8	6	4	3	2	1

Confidence Level
60(%): two-tailed t test
80(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	2	1	1	1	1	1	1	1	1	1	1	1
2	4	2	1	1	1	1	1	1	1	1	1	1
4	13	4	2	1	1	1	1	1	1	1	1	1
6	27	8	2	1	1	1	1	1	1	1	1	1
8	47	13	3	2	1	1	1	1	1	1	1	1
10	72	19	4	2	1	1	1	1	1	1	1	1
20	284	72	13	4	2	2	2	1	1	1	1	1
30	638	160	27	8	4	3	2	2	1	1	1	1
40	1134	284	47	13	6	4	3	2	2	2	1	1
50	1771	443	72	19	9	6	4	3	2	2	1	1
100	7084	1771	284	72	33	19	13	9	6	4	2	2

(Continued)

TABLE A-1.

Confidence Level
70(%): two-tailed t test
85(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	2	1	1	1	1	1	1	1	1	1	1	1
2	6	2	1	1	1	1	1	1	1	1	1	1
4	19	6	2	1	1	1	1	1	1	1	1	1
6	42	11	3	2	1	1	1	1	1	1	1	1
8	74	19	4	2	2	1	1	1	1	1	1	1
10	115	28	6	2	2	2	1	1	1	1	1	1
20	430	115	19	6	3	2	2	2	1	1	1	1
30	967	242	42	11	6	4	3	2	2	2	1	1
40	1719	430	74	19	9	6	4	3	2	2	1	1
50	2686	672	115	28	13	8	6	4	3	2	2	1
100	10742	2686	430	115	52	28	19	13	8	6	3	2

Confidence Level
80(%): two-tailed t test
90(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	3	2	1	1	1	1	1	1	1	1	1	1
2	8	3	2	1	1	1	1	1	1	1	1	1
4	28	8	2	2	1	1	1	1	1	1	1	1
6	61	16	4	2	2	1	1	1	1	1	1	1
8	107	28	6	3	2	2	1	1	1	1	1	1
10	165	43	8	3	2	2	2	1	1	1	1	1
20	657	165	28	8	4	3	2	2	2	2	1	1
30	1479	370	61	16	8	5	4	3	2	2	2	1
40	2628	657	107	28	13	8	6	4	3	2	2	2
50	4106	1027	165	43	20	12	8	6	4	3	2	2
100	16424	4106	657	165	75	43	28	20	12	8	5	3

(Continued)

TABLE A-1.

Confidence Level
90(%): two-tailed t test
95(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	5	2	2	1	1	1	1	1	1	1	1	1
2	13	5	2	2	1	1	1	1	1	1	1	1
4	46	13	4	2	2	2	1	1	1	1	1	1
6	100	27	6	3	2	2	2	2	1	1	1	1
8	174	46	9	4	3	2	2	2	2	1	1	1
10	271	70	13	5	3	3	2	2	2	2	1	1
20	1083	271	46	13	7	5	3	3	2	2	2	2
30	2435	609	100	27	13	8	6	5	3	3	2	2
40	4329	1083	174	46	21	13	9	7	5	3	2	2
50	6764	1691	271	70	32	19	13	10	6	5	3	2
100	27055	6764	1083	271	121	70	46	32	19	13	7	3

Confidence Level
95(%): two-tailed t test
97.5(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	6	3	2	2	1	1	1	1	1	1	1	1
2	18	6	3	2	2	2	1	1	1	1	1	1
4	64	18	5	3	2	2	2	2	2	1	1	1
6	139	37	8	4	3	2	2	2	2	2	1	1
8	246	64	12	5	3	3	2	2	2	2	2	1
10	385	99	18	6	4	3	3	2	2	2	2	2
20	1537	385	64	18	9	6	5	4	3	3	2	2
30	3458	865	139	37	18	11	8	6	5	4	3	2
40	6147	1537	246	64	30	18	12	9	6	5	3	3
50	9604	2401	385	99	45	27	18	13	9	6	4	3
100	38416	9604	1537	385	171	99	64	46	27	18	9	6

(Continued)

TABLE A-1.

Confidence Level
98(%): two-tailed t test
99(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	8	4	2	2	2	2	2	2	1	1	1	1
2	25	9	3	2	2	2	2	2	2	2	1	1
4	90	25	6	3	3	2	2	2	2	2	2	2
6	195	52	11	5	3	3	2	2	2	2	2	2
8	347	90	17	7	4	3	3	2	2	2	2	2
10	542	136	25	9	5	4	3	3	2	2	2	2
20	2165	542	90	25	13	9	6	5	4	3	3	2
30	4871	1218	195	52	25	15	11	9	6	5	3	3
40	8659	2165	347	90	42	25	17	13	9	7	4	3
50	13530	3383	542	136	63	37	25	18	12	9	5	4
100	54119	13530	2165	542	241	136	90	63	37	25	13	8

Confidence Level
99(%): two-tailed t test
99.5(%): one-tailed t test
Precision p(%)

CV (%)	1	2	5	10	15	20	25	30	40	50	75	100
1	10	5	3	2	2	2	2	2	2	2	1	1
2	31	10	4	3	2	2	2	2	2	2	2	2
4	110	31	8	4	3	3	3	2	2	2	2	2
6	239	64	13	6	4	3	3	3	3	2	2	2
8	425	110	21	8	5	4	3	3	3	3	2	2
10	664	166	31	10	6	5	4	4	3	3	2	2
20	2655	664	110	31	16	10	8	6	5	4	3	3
30	5973	1493	239	64	31	19	13	10	7	6	4	3
40	10618	2655	425	110	51	31	21	16	10	8	5	4
50	16590	4148	664	166	78	46	31	22	14	10	6	5
100	66358	16590	2655	664	295	166	110	78	46	31	16	10

APPENDIX B
TABLES FOR USE IN CALCULATING CONFIDENCE AND TOLERANCE LIMITS AND JUDGING THE VALIDITY OF MEASUREMENTS

A series of tables are presented which can be used to calculate confidence intervals for averages, percentiles of the t-distribution, the standard deviation, the tolerance interval for individuals and critical values for discarding invalid measurements.

TABLE B-1. PERCENTILES OF THE t DISTRIBUTION

	Confidence Level (%):$1-\alpha/2$ for two-tailed test							
	20	30	60	80	90	95	98	99
	Confidence Level (%):$1-\alpha$ for one-tailed test							
df	60	70	80	90	95	97.5	99	99.5
1	.325	.727	1.376	3.078	6.314	12.706	31.821	63.657
2	.289	.617	1.061	1.886	2.920	4.303	6.965	9.925
3	.277	.584	.978	1.638	2.353	3.182	4.541	5.641
4	.271	.569	.941	1.533	2.132	2.776	3.747	4.604
5	.267	.559	.920	1.476	2.015	2.571	3.365	4.032
6	.265	.553	.906	1.440	1.943	2.447	3.143	3.707
7	.263	.549	.896	1.415	1.895	2.365	2.998	3.499
8	.262	.546	.889	1.397	1.860	2.306	2.896	3.355
9	.261	.543	.883	1.383	1.833	2.262	2.821	3.250
10	.260	.542	.879	1.372	1.812	2.228	2.764	3.169
11	.260	.540	.876	1.363	1.796	2.201	2.718	3.106
12	.259	.539	.873	1.356	1.782	2.179	2.681	3.055
13	.259	.538	.870	1.350	1.771	2.160	2.650	3.012
14	.258	.537	.868	1.345	1.761	2.145	2.624	2.977
15	.258	.536	.866	1.341	1.753	2.131	2.602	2.947
16	.258	.535	.865	1.337	1.746	2.120	2.583	2.921
17	.257	.534	.863	1.333	1.740	2.110	2.567	2.898
18	.257	.534	.862	1.330	1.734	2.101	2.552	2.878
19	.257	.533	.861	1.328	1.729	2.093	2.539	2.861
20	.257	.533	.860	1.325	1.725	2.086	2.528	2.845
21	.257	.532	.859	1.323	1.721	2.080	2.518	2.831
22	.256	.532	.858	1.321	1.717	2.074	2.508	2.819
23	.256	.532	.858	1.319	1.714	2.069	2.500	2.807
24	.256	.531	.857	1.318	1.711	2.064	2.492	2.797
25	.256	.531	.856	1.316	1.708	2.060	2.485	2.787
26	.256	.531	.856	1.315	1.706	2.056	2.479	2.779
27	.256	.531	.855	1.314	1.703	2.052	2.473	2.771
28	.256	.530	.855	1.313	1.701	2.048	2.467	2.763
29	.256	.530	.854	1.311	1.699	2.045	2.462	2.756
30	.256	.530	.854	1.310	1.697	2.042	2.457	2.750
40	.255	.529	.851	1.303	1.684	2.021	2.423	2.704
60	.254	.527	.848	1.296	1.671	2.000	2.390	2.660
120	.254	.526	.845	1.289	1.658	1.980	2.358	2.617
oc	.253	.524	.842	1.282	1.645	1.960	2.326	2.576

Table B-2. CI=$\hat{\bar{X}} \pm A(\Sigma R)$. *Confidence Interval for Averages**

		n								
Prob.	*k*	2	3	4	5	6	7	8	9	10
0.05	1	6.36	1.30	0.719	0.505	0.402	0.336	0.291	0.256	0.232
0.01		31.9	3.00	1.36	0.865	0.673	0.514	0.430	0.379	0.338
0.05	2	0.879	0.316	0.206	0.154	0.125	0.106	0.093	0.084	0.076
0.01		2.11	0.474	0.312	0.227	0.179	0.150	0.131	0.116	0.105
0.05	3	0.360	0.156	0.104	0.079	0.065	0.056	0.049	0.044	0.040
0.01		0.660	0.273	0.150	0.112	0.091	0.077	0.068	0.060	0.054
0.05	4	0.210	0.096	0.065	0.050	0.042	0.036	0.032	0.028	0.026
0.01		0.350	0.142	0.092	0.070	0.057	0.048	0.043	0.038	0.035
0.05	5	0.140	0.066	0.046	0.035	0.030	0.025	0.022	0.020	0.018
0.01		0.226	0.095	0.063	0.049	0.040	0.034	0.030	0.027	0.025
0.05	6	0.102	0.050	0.034	0.027	0.022	0.019	0.017	0.015	0.014
0.01		0.157	0.070	0.047	0.036	0.030	0.026	0.023	0.020	0.019
0.05	7	0.079	0.039	0.027	0.021	0.018	0.015	0.013	0.012	0.011
0.01		0.117	0.055	0.037	0.029	0.024	0.020	0.018	0.016	0.015
0.05	8	0.063	0.032	0.022	0.017	0.014	0.012	0.011	0.010	0.009
0.01		0.094	0.044	0.030	0.023	0.019	0.016	0.014	0.013	0.012
0.05	9	0.053	0.027	0.018	0.014	0.012	0.010	0.009	0.008	0.007
0.01		0.076	0.036	0.025	0.019	0.016	0.014	0.012	0.011	0.010
0.05	10	0.044	0.023	0.016	0.012	0.010	0.009	0.008	0.007	0.006
0.01		0.064	0.031	0.021	0.016	0.014	0.012	0.010	0.009	0.008

*Given *k* subgroups of *n* numbers, the confidence interval is $\bar{X} \pm A(\Sigma R)$.

From Bauer, 1971.

Table B-3. Single Classification Factor (c_1) to Estimate Standard Deviation from Range, and Equivalent Degrees of Freedom (f)[a]

$$s = \frac{\bar{R}}{c_1}$$

	n																	
	2		3		4		5		6		7		8		9		10	
k	f	c_1	f	c_1	f	c_1	f	c_1	f	c_1	f	c_1	f	c_1	f	c_1	f	c_1
1	1.0	1.41	2.0	1.91	2.9	2.24	3.8	2.48	4.7	2.67	5.5	2.83	6.3	2.96	7.0	3.08	7.7	3.18
2	1.9	1.28	3.8	1.81	5.7	2.15	7.5	2.40	9.2	2.60	10.8	2.77	12.3	2.91	13.8	3.02	15.1	3.13
3	2.8	1.23	5.7	1.77	8.4	2.12	11.1	2.38	13.6	2.58	16.0	2.75	18.3	2.89	20.5	3.01	22.6	3.11
4	3.7	1.21	7.5	1.75	11.2	2.11	14.7	2.37	18.1	2.57	21.3	2.74	24.4	2.88	27.3	3.00	30.1	3.10
5	4.6	1.19	9.3	1.74	13.9	2.10	18.4	2.36	22.6	2.56	26.6	2.73	30.4	2.87	34.0	2.99	37.5	3.10
6	5.5	1.18	11.1	1.73	16.6	2.09	22.0	2.36	27.1	2.56	31.9	2.73	36.4	2.87	40.8	2.99	45.0	3.10
7	6.4	1.17	12.9	1.72	19.4	2.08	25.6	2.35	31.5	2.56	37.1	2.73	42.5	2.87	47.6	2.98	52.4	3.09
8	7.2	1.16	14.8	1.71	22.1	2.08	29.3	2.35	36.0	2.55	42.4	2.72	48.5	2.86	54.3	2.98	59.8	3.09
9	8.1	1.15	16.6	1.70	24.9	2.07	32.9	2.34	40.5	2.55	47.7	2.72	54.5	2.86	61.1	2.98	67.3	3.09
10	9.0	1.14	18.4	1.69	27.6	2.07	36.5	2.34	44.9	2.55	52.9	2.72	60.6	2.86	67.8	2.98	74.8	3.09

From Bauer, 1971.

Table B-4. $TI = \bar{X} \pm I(\Sigma R)$. *Tolerance Interval for Individuals*

		n								
Prob.	***k***	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
0.05	1	8.99	2.25	1.44	1.13	0.985	0.889	0.823	0.768	0.734
0.01		45.1	5.20	2.72	1.93	1.65	1.36	1.22	1.14	1.07
0.05	2	1.76	0.774	0.583	0.487	0.433	0.397	0.372	0.356	0.340
0.01		4.22	1.16	0.882	0.718	0.620	0.561	0.524	0.492	0.470
0.05	3	0.882	0.486	0.360	0.306	0.276	0.257	0.240	0.229	0.219
0.01		1.62	0.819	0.520	0.434	0.386	0.353	0.333	0.312	0.296
0.05	4	0.594	0.332	0.260	0.224	0.206	0.190	0.181	0.168	0.164
0.01		0.990	0.492	0.368	0.313	0.279	0.254	0.243	0.228	0.221
0.05	5	0.443	0.256	0.206	0.175	0.164	0.148	0.139	0.134	0.127
0.01		0.715	0.368	0.282	0.245	0.219	0.201	0.190	0.181	0.177
0.05	6	0.353	0.212	0.166	0.148	0.132	0.123	0.118	0.110	0.108
0.01		0.544	0.297	0.230	0.197	0.180	0.168	0.159	0.147	0.145
0.05	7	0.296	0.179	0.143	0.124	0.117	0.105	0.097	0.095	0.092
0.01		0.438	0.252	0.196	0.172	0.156	0.140	0.135	0.127	0.124
0.05	8	0.252	0.157	0.124	0.108	0.097	0.090	0.088	0.085	0.080
0.01		0.376	0.216	0.170	0.145	0.132	0.120	0.112	0.110	0.108
0.05	9	0.225	0.140	0.108	0.094	0.088	0.079	0.076	0.072	0.066
0.01		0.322	0.187	0.150	0.127	0.118	0.111	0.101	0.099	0.095
0.05	10	0.197	0.126	0.101	0.085	0.077	0.075	0.072	0.066	0.060
0.01		0.286	0.170	0.133	0.113	0.108	0.100	0.089	0.085	0.080

$$I = \frac{t}{kc_1}$$

From Bauer, 1971.

Table B-5. Critical Values for Discarding Invalid Measurements

n	t_i
3	1.53
4	1.05
5	0.86
6	0.76
7	0.69
8	0.64
9	0.60
10	0.58
11	0.56
12	0.54
13	0.52
14	0.51
15	0.50
20	0.46

The probability is approximately 0.95 that if $t_i = |X - \bar{X}|/R$ is greater than tabulated t_i the value being investigated is invalid.

From Bauer, 1971.